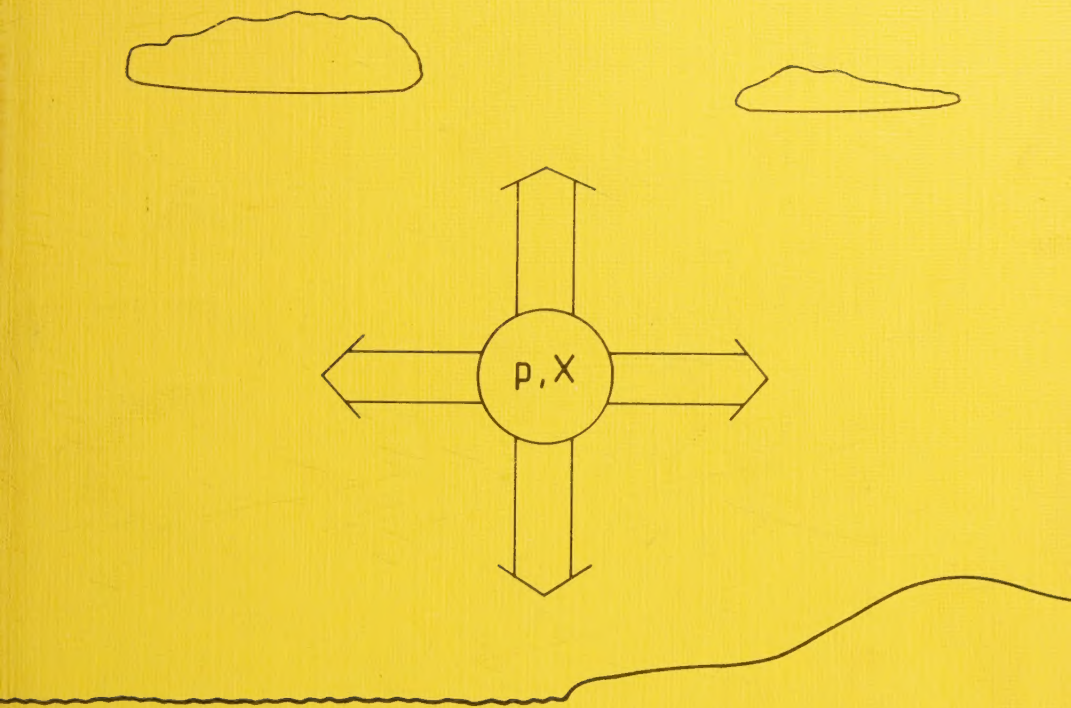




APPLICATIONS OF PARTICLE INDUCED X-RAY EMISSION ANALYSIS TO AMBIENT AEROSOL STUDIES-

long range transport, composition and sources

HANS LANNEFORS

— *Lund 1982.*



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APPLICATIONS OF PARTICLE INDUCED X-RAY EMISSION ANALYSIS TO AMBIENT AEROSOL STUDIES-

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HANS LANNEFORS



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Title and subtitle Applications of Particle Induced X-Ray Emission Analysis to Ambient Aerosol Studies- Long range transport, composition and sources.	
Abstract The characteristics of Particle Induced X-ray Emission (PIXE) analysis in conjunction with different ambient aerosol samplers have been studied. Correction factors have been calculated for homogeneous and inhomogeneous rural and urban aerosol samples. X-ray absorption is most important for elements up to vanadium, while the proton energy loss correction dominates for heavier elements (K_{α} X-rays considered). The Nuclepore two stage filter sampler provided the most useful combination of the resolution and particle size fractionation in urban, rural and remote environments. The PIXE-analysis technique in combination with different samplers was employed in aerosol composition studies in rural and remote environments. Particular emphasis was laid on studies of aerosol long range transport. Based on air mass trajectory analysis and aerosol composition measurements the foreign contribution in southern Sweden was estimated to be 70 - 80% for S and Pb but only 30 - 50% for V and Ni. The spatial and temporal extension of a long range transport episode was studied using high time resolution continuous filter samplers in a network in southern Sweden. The variation in the concentration levels of sulphur agreed well with changes in the air mass history. Arctic summer elemental concentration levels as measured during the Swedish YMER-80 icebreaker expedition were typically one order of magnitude lower than Arctic winter levels. The combination of chemical information, optical properties and size distribution data supports the hypothesis of long range transport of air pollution into the Arctic especially during the winter. This takes place during the winter season because the Polar front is further south making conditions for long range transport up to the Arctic more favourable.	
Key words PIXE, X-ray absorption, proton energy loss, ambient aerosol composition, sulphur, heavy metals, size distribution, long range transport air mass trajectory, background aerosol, Arctic aerosol	
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April 23, 1982

to my family

APPLICATIONS OF PARTICLE INDUCED X-RAY EMISSION ANALYSIS TO AMBIENT AEROSOL STUDIES

Long range transport, composition and sources

by

HANS LANNEFORS

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SUMMARYIntroduction

In recent years the first signs of globally increasing levels of air pollution have been confirmed. The anthropogenic air pollution sources are confined to relatively small land areas thus resulting in drastically increased levels in and near these regions. In order to understand and foresee possible effects in e.g. medicine, biology, ecology and climatology; the sources, transport mechanisms and sinks of air pollution need to be known in some detail. During the last decade much work has been initiated to increase the knowledge of ambient aerosol behaviour and to establish baseline concentrations for future comparisons. Different source types have to be characterised to make possible the determination of the origin and effect of different natural and anthropogenic aerosol components. Models predicting transport and deposition of ambient aerosols require considerable amounts of experimental information to be constructed, validated and used.

The introduction in 1970 of a fast multi-elemental technique (PIXE) for analysis of elements heavier than aluminum facilitated large scale aerosol studies. The properties of PIXE (described later) make it very useful for producing large amounts of information concerning aerosol composition. However, to take advantage of these properties new strategies and routines for aerosol sampling, data handling and interpretation had to be developed.

Depending on the aim and the prevailing aerosol concentrations different sampling techniques in combination with PIXE analysis may be chosen to obtain the optimum system. The characteristics of the PIXE method applied to different types of samples are discussed in paper I. Information on aerosol source types and dominating source areas is gained using a combination of size fractionating samplers and a multi-elemental technique. This is made possible by the PIXE technique's small sample requirements thus allowing a time resolution sufficient for meteorological interpretation (paper II). Even higher time resolution is obtained using a non-fractionating continuous sampler. By simultaneously using these samplers in a network, information concerning the spatial distribution of aerosol constituents as a function of meteorological parameters has been studied (paper III). The combination of elemental concentrations as analysed by PIXE, and other physical and chemical aerosol parameters has enabled the characterisation of a remote (Arctic) aerosol and identification of possible sources contributing to its composition (papers IV and V).

The PIXE-method

Particle induced X-ray emission (PIXE) analysis is a fast multi-elemental technique with the capability of quantifying elements heavier than aluminum. Detection limits in a 3-5 minute routine irradiation are typically in the ng-range for a 10 µg sample. Furthermore PIXE is an absolute method requiring no standards when using a calibrated set-up. However, to continuously control the results, standards are run along with each batch of samples. The accuracy for thin samples are in the 5% range (ref 1). Samples of intermediate thickness (as discussed in paper I) require corrections which could considerably decrease the accuracy of the analytical results.

The physical principle of the PIXE method is based on accelerated charged particles (protons or α -particles) in the MeV/u range bombarding the sample to be analysed. Thus inner shell vacancies in the atoms of the sample are created. When electrons from the outer shells fill the vacancies, X-rays with energies characteristic of the atoms may be emitted. By measuring the intensity and energy of the X-rays, the sample composition can be determined for elements with atomic numbers greater than 13.

Experimentally the PIXE-analyses are performed in a chamber as shown in figure 1. The sample, mounted in a slide frame is placed in vacuum and irradiated by charged particles accelerated by an electrostatic accelerator or a cyclotron. The area analysed is determined by circular collimators and a beam current in the 1-200 nA range is normally used. A set of interchangeable absorbers to reduce the low energy X-ray intensity is mounted in front of the semi-conductor detector which measures the X-ray energies. The detector signals are amplified and later processed and stored in a multichannel analyser. The resulting X-ray spectrum as shown in figure 2 contains X-rays from more than 10 elements which are simultaneously quantified.

The PIXE analysis technique was developed in our laboratory and described by Johansson, Akselsson and Johansson in 1970 (ref 2). The PIXE-method has found numerous applications and is now in use in more than 200 laboratories throughout the world. The proceedings of two international conferences (ref 3 and 4) held in Lund in 1976 and 1980 contain reports and documentation of various applications and their usefulness.

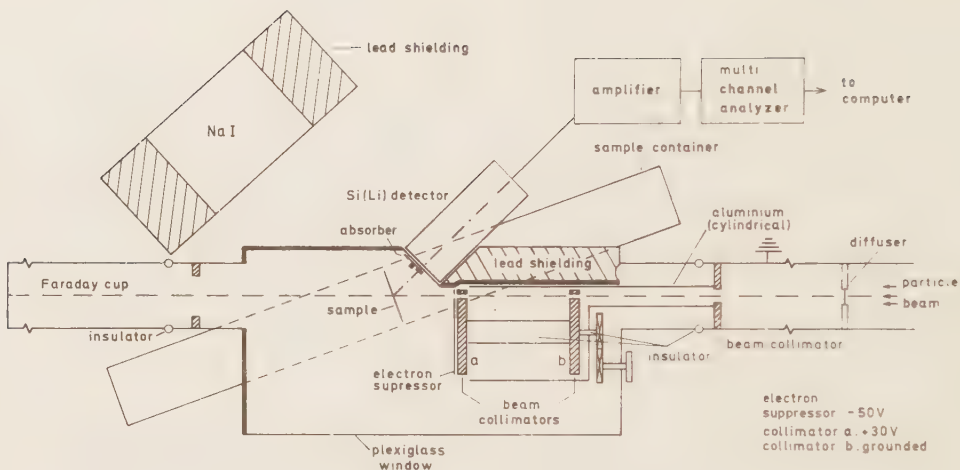


Figure 1. Experimental arrangement.

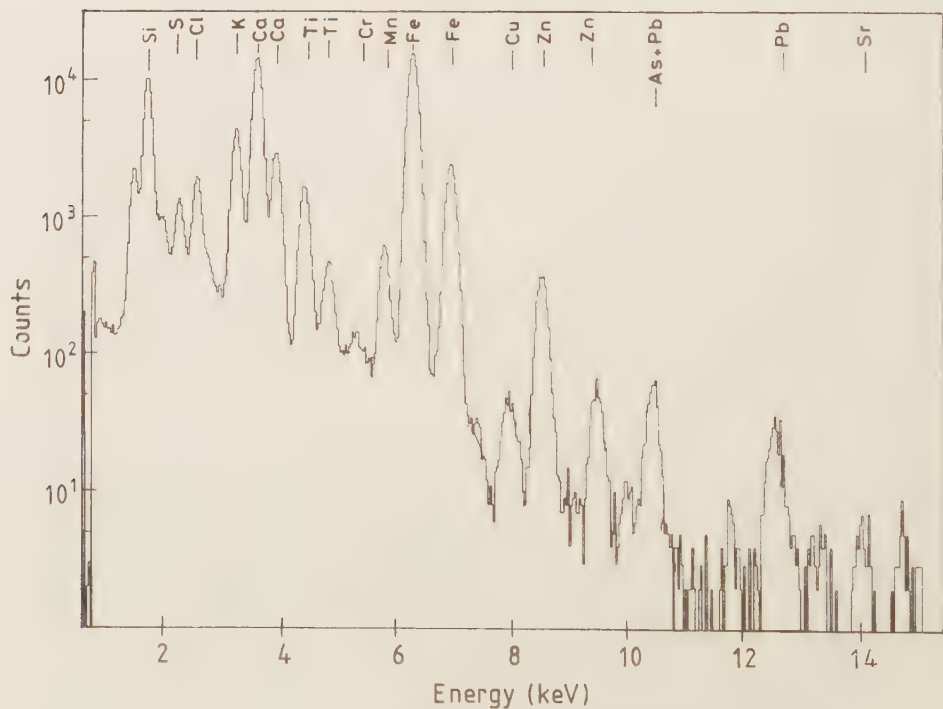


Figure 2. X-ray spectrum of an ambient aerosol sample.

Dissertation

The aim of this work in applying the PIXE-analysis technique to ambient aerosol studies was:

- a) to demonstrate large scale atmospheric aerosol applications by utilising a multi-elemental technique capable of processing a large number of samples,
- b) to establish atmospheric aerosol composition baseline levels,
- c) to study the influence of long range aerosol transport at rural and remote locations, and
- d) to identify source types and source areas of importance for the aerosol composition in southern Sweden.

Paper I

The Pixe-analysis technique has proven to be useful in combination with many different samplers. However care has to be taken in order to perform accurate analyses. Ambient aerosol samples thicker than a few tenths of mg/cm^2 experience 10-20% X-ray self absorption for the lighter elements e.g. P, S and Cl. Especially non-uniform samples such as cascade impactor, cone formed deposits very easily exceed a thickness where corrections are necessary. Comparing sampling times needed for four different samplers revealed that the Nuclepore two stage filter sampler generally gave the highest time resolution. With respect to average elemental concentrations in urban, rural and remote environments the sampling times necessary to exceed detection limits by a factor of 10 were found to be 15 minutes, 6 hours and 2 weeks respectively. Interpretation of short-time aerosol concentration variations in urban environments is thus possible while in the remote environment only trends on a longer time scale e.g. seasonal and yearly trends can be studied.

Paper II

In order to correlate future changes in air pollution emissions to an altered atmospheric aerosol composition, baseline concentrations must be established. Measurements during a one year cycle were therefore undertaken in a rural area in southern central Sweden. More than one hundred samples were collected using a Battelle-type cascade impactor and subsequently analysed by PIXE in Copenhagen and Lund.

The sulphur and heavy metal concentration levels were found to be one order of magnitude or more lower than in central Europe but considerably higher than the relatively high Arctic winter values (see paper IV). Relating the elemental concentrations to the history of the air mass reveals one order of magnitude higher average concentrations of the anthropogenic components in air masses having traversed central Europe or the U.K. compared with northerly air masses. Using a simple box model the foreign contribution was estimated to be 70-80% for S and Pb but lower for Ni and V. A considerable seasonal variation was found with the soil derived components i.e. K, Ca, Ti and Fe being highest in spring while the anthropogenic components i.e. S, V, Ni, Cu, Zn and Pb were highest in winter. Rough estimates of dry deposition velocities in the different cascade impactor size fractions were used to calculate the resulting elemental dry deposition velocities. Compared with measured wet deposition the calculated dry deposition is lower for most of the elements.

Paper III

More detailed information about the long range transport of sulphur to southern Scandinavia was obtained using a sampling network designed to give a high spatial and temporal resolution. Florida State University (FSU) time sequence filter samplers were placed at five rural and one urban location in southern Sweden and operated simultaneously. PIXE-analysis performed at FSU revealed time series of sulphur evaluated with the help of surface weather maps and 850 mbar backtrajectories. Two episodes drawing up polluted air masses from central Europe were clearly identified both meteorologically and by increased sulphur-levels. The spatial extensions of an episode could also be followed by combining the sulphur time series obtained at the different sampling locations. The ratios of S to V and Ni, respectively, were found to be indicators of recent emissions from nearby sources. These ratios also proved to be useful in identifying a few cases of local influence.

Paper IV

Clear indications of air pollution in the Arctic have been found in Alaska. This anthropogenic influence is apparently strongest in winter when the meteorological conditions are more favourable for long range transport from midlatitudinal source areas. In a late winter campaign on Spitsbergen a number of physical and chemical aerosol parameters were measured simultaneously. Great

Average late winter concentrations were typically one order of magnitude higher than summer Greenland data and one to two orders of magnitude higher than austral summer South Pole data. The optical data were inverted (transferred to particle size distributions) making some assumptions about particle refractive index and density. The inverted fine and coarse particle mode concentrations agreed well with those obtained from chemical measurements. The combination of chemical composition, optical properties and size distribution data supports the hypothesis of long range air pollution transport into the Arctic.

Paper V

Physical and chemical properties of the Arctic summer aerosol were measured in cooperation with the department of Meteorology in Stockholm during the Ymer-80 icebreaker expedition to the Norwegian Arctic. By combining information gained about the aerosol size distribution and chemical composition, occurrences with possible local contamination could be avoided or later excluded. Emissions from Arctic settlements were found to contribute only in the Aitken particle range and had no influence on the accumulation mode.

Meteorologically the Arctic is decoupled from the influence of midlatitudinal air masses during the summer when the polar front is often found far north of the Scandinavian peninsula. Generally very low concentrations of known anthropogenic components should be expected and were also recorded, often one order of magnitude lower than winter values as measured at Spitsbergen. However, air masses probably originating in large European source areas were recorded on a few occasions and were characterised by high concentrations of soot, sulphur and heavy metals. The concept of "background concentrations" as assumed to be found in the Arctic was investigated. These "background concentrations" were found to be low but variable, and determined by the relative strength of active sink and source mechanisms in combination with the sampling time resolution.

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Paper I

COMPARISON OF SOME AMBIENT AEROSOL SAMPLERS IN COMBINATION WITH PIXE-ANALYSIS

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ABSTRACT

In the PIXE-analysis of aerosols many different kinds of samplers combined with different types of filters and backings are employed. In this investigation sample thickness corrections, detection limits and required sampling times in different environments have been studied for four different samplers i.e. two total filter samplers, a two stage filter sampler and a cascade impactor. The samplers have been used with filters made by Ghia, Millipore and Nuclepore and backings of polystyrene film, respectively. The calculations are based on the accumulation mode aerosol (particles in the 0.05-2 μm diameter range) composition.

Sampling times resulting in detection limits 10 times lower than assumed aerosol concentrations ranged from a quarter of an hour in urban, a quarter of a day in rural to two weeks in remote environments. These sampling times are calculated under the requirement that at least one element representing each of the following sources were detected: fossil fuel combustion (S, V and Ni), leaded petrol combustion (Br and Pb) and general industrial activities (Cr, Cu and Zn). Generally the two stage filter sampler employed with Nuclepore filters yields the highest time resolution when specific flow rate, thickness and substrate impurities are taken into consideration.

Thickness corrections based on a proton energy of 2.55 MeV and typical ambient urban and rural aerosol matrices show that light elements such as P, S and Cl where the X-ray self absorption effect is most important require a 10 - 20% correction with a uniform deposit thickness of about 0.5 mg/cm^2 and a non-uniform (conical) deposit thickness of about 1 mg/cm^2 . For elements heavier than vanadium (K X-rays) the proton energy loss correction dominates. Sampling times resulting in the above mentioned deposit thicknesses were shortest for the cascade impactor while the Millipore and Nuclepore filter samplers were least critical in this respect.

INTRODUCTION

Aerosol composition studies in general and ambient aerosol studies in particular have been a main application of particle induced X-ray emission (PIXE) analysis ever since it was introduced by Johansson et. al. in 1970. Multi-elemental capacity, high sensitivity for small samples and low detection limits for many elements of hygienic interest thus proved to be a favourable combination. The analytical applications of PIXE were reviewed in 1976 by Johansson and Johansson and are further exposed in the proceedings of the first and second international conference on PIXE and its analytical applications (Editor S.A.E. Johansson 1977 and 1981).

PIXE has been the analytical tool for numerous aerosol composition studies in urban, rural and remote locations. Some of these studies are described in the earlier mentioned conference proceedings. The high analytical capacity has facilitated the undertaking of large scale studies e.g. (Flocchini et al 1976, Winchester 1981 and Lannefors et al 1982). Many different aerosol samplers have been found suitable for combination with PIXE-analysis, others have been adapted or developed for the special sample demands as posed by the PIXE-technique. There now exists a wide spectrum of samplers giving possibilities for aerosol studies with different time, particle size and spatial resolution. The high sensitivity of the PIXE-method giving detection limits down to tenths of a ng in samples smaller than approximately 100 µg enables the use of low volume samplers requiring only small and inexpensive pumps which is favourable in larger multisampler programs.

Since the development of PIXE a great deal of experience concerning its application to ambient aerosol analysis has been gained. In order to obtain useful and reliable results great caution has to be taken in the procedure of sampling and analysis. Large errors can easily be introduced e.g. by overloading the samplers. This can also cause considerable X-ray self absorption and proton energy loss. In this paper parameters of importance when performing ambient aerosol sampling are discussed, assuming certain aerosol compositions and concentration levels and with respect to lower limits of detection.

DEMANDS ON SAMPLES FOR PIXE-ANALYSIS

In order to create a base for further discussions some analytical properties of importance are shortly mentioned and referenced. All figures given refer to a 3-5 minute sample bombardment using protons of 2.55 MeV energy and measuring elements heavier than silicon. A Kevex 80 mm² Si(Li) detector collimated to an effective area of 28 mm² was used and placed at a distance of 40 mm from the sample at an angle of 135 degrees to the beam. The sample normal had an angle of 157.5 degrees to the beam. The exit window of the irradiation chamber is a beryllium foil having a thickness as great as 109 µm in order to prevent scattered protons from entering the detector.

To make quantitative analysis possible the sample must either have an area smaller than the beam or consist of a uniform layer of which only a part will be irradiated and thus representing the whole sample. In the first case the proton beam intensity must be uniform. This can be obtained either by scanning the beam in x and y directions across the sample or by introducing a diffuser foil into the beam. In the Lund PIXE arrangement (see Fig 1) a 1 mg/cm² gold foil is used as a diffuser (Malmqvist et al in press). Beam diameters in the range of 1 to 13 mm may be chosen.

For samples of non-negligible thickness the proton energy loss will decrease the X-ray production and introduce an error which is largest for the heavier elements. X-rays produced in the sample will be absorbed on their way out of the sample. This self absorption loss increases with decreasing X-ray energy thus being most serious for the lighter elements (Johansson et al 1975). To correct for both proton energy loss and X-ray self absorption the sample matrix, density, form and thickness must be known.

Inserting the sample into vacuum (10^{-4} torr) may cause volatile elements to evaporate. This effect may also be enhanced by proton bombardment during analysis, which causes heating of the sample. The heating effect increases with the added thickness of sample and backing. Losses of volatile elements can be kept at negligible levels in the PIXE-analysis of ambient aerosols (Cahill 1973 and Johansson et al 1975). However, at high beam intensities (>200 nA/cm²) on heavily loaded Millipore filters we have seen significant losses of Br. Hansen et al (1980) have found losses of sulphur in aerosol samples which they attribute to radiation induced chemical reactions forming volatile compounds. In some studies in which we have participated sulphur has been analysed both wet chemically and by PIXE (different samples but taken

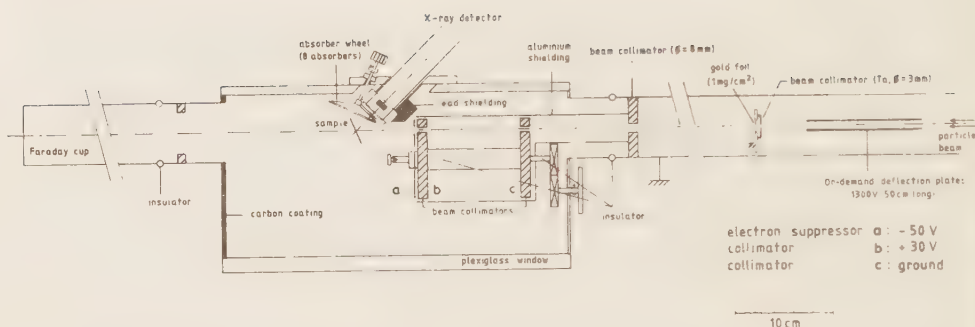


Fig 1. The Lund experimental arrangement. (From Malmqvist et al (in press).)

simultaneously) e.g. Heintzenberg et al (1981). The agreement has been satisfactory, deviations between individual samples typically being below 20%. However these studies were undertaken at rural and remote locations while those of Hansen et al (1980) included sampling in or near smoke plumes.

The ideal sampling system with respect to the properties of the PIXE-method produces a uniform sample with an area somewhat larger than a comfortable beam size (5-10 mm). The thickness should not exceed values where corrections for elements of interest become significant compared with other uncertainties experienced i.e. from the sampling system and the analytical precision. If samples of infinite thickness (larger than 12 to 13 mg/cm^2 for 2.55 MeV protons in the matrices described later) can be obtained this would result in lower detection limits with approximately the same accuracy as for the very thin samples (Carlsson and Akselsson 1981). However, in this case the total sample mass must be known. Using commercially available membrane filters, clogging of the filter will probably occur before such thicknesses are reached.

DETECTION LIMITS OF BACKINGS AND FILTERS

To obtain sufficient time resolution we have tried to find optimal sampling and analysis conditions. Two different non segregating total samplers, a two stage filter sampler (Cahill et al 1979) and a seven stage Battelle-type

cascade impactor (Mitchell and Pilcher 1959) are presently used at our laboratory in conjunction with PIXE-analysis. As total filters we normally use Ghia (Zefluor) or Millipore filters (see table 1). The former filter is mounted in a modified 25 mm Nuclepore holder where the exposed surface is limited to 28 mm^2 by a conical inlet pressed towards the filter which is supported by a soft backing. The Millipore filter is normally mounted in a standard Millipore cassette. The two stage filter sampler consists of a 25 mm Nuclepore filter ($8 \text{ }\mu\text{m}$ pore diameter) and a 13 mm Nuclepore filter ($0.4 \text{ }\mu\text{m}$ pore diameter with a soft backing) mounted in Nuclepore and Millipore holders respectively, coupled in series. This combination enhances the analytical detectability of the second stage while keeping the face velocity of the first stage at a level so as to obtain a $2\text{-}3 \text{ }\mu\text{m}$ diameter 50% cut off (Cahill et al 1979). The first filter collecting mainly coarse particles, will not be discussed further since this discussion is to be confined to the accumulation mode (particles in the $0.05\text{-}2 \text{ }\mu\text{m}$ diameter range) aerosol composition when size fractionating samplers are considered. The impaction surfaces in the cascade impactor consist of 25 mm glass discs coated with polystyrene with paraffin evaporated onto one side. The finest fraction ($<0.25 \text{ }\mu\text{m}$ particle diameter) is collected using a $0.4 \text{ }\mu\text{m}$ pore diameter Nuclepore filter. The properties of filters and backing materials discussed here are summarized in table 1.

Table 1 Properties of filters and impaction backings used in conjunction with PIXE-analysis

Filter/Backing	Material	Thickness	Pore diameter
		(mg/cm^2)	(μm)
Ghia* (Zefluor)	Teflon	0.3	2
Millipore AA	Mixed cellulose acetate	5	0.8
Nuclepore	Polycarbonate	1	0.4
Impactor backing	Polystyrene + paraffin**	0.05	-

* Ghia corporation, Pleasanton, California, USA.

** Paraffin evaporated onto the polystyrene

Ideally, for PIXE analysis, the sampling substrates should be very thin to minimize the background from electron and proton bremsstrahlung. It is also important that the content of elements (e.g. F, Na, Li and B) having high yields of gamma-rays is low. If the substrates contain any impurities of the elements to be analysed, their content should be as constant as possible in order to give low effective (the blank content variation taken into consideration) limits of detection.

The sampling and analysis conditions of the four substrates are described in table 2. The irradiated area was determined by the deposit size and form which was dependent of sampler and filter porosity. The Ghia and polystyrene substrates were analysed as point samples i.e. using a beam area larger than the deposit area. These substrates are not self-supporting during handling and sampling and therefore have a soft backing and a glass disc support, respectively, which are removed prior to analysis. The elasticity of the teflon filter often causes the exposed area to change when the filter is mounted for analysis. This results in an unknown area for normalization if using a beam smaller than the exposed area. The cascade impactor produces non-uniform samples from the impinging particles. Tests have been undertaken to determine the smallest beam collimator that includes the whole deposit. As seen in table 2 the Millipore and Nuclepore filters have a uniform deposit area large enough to be analysed with a beam smaller than the exposed area.

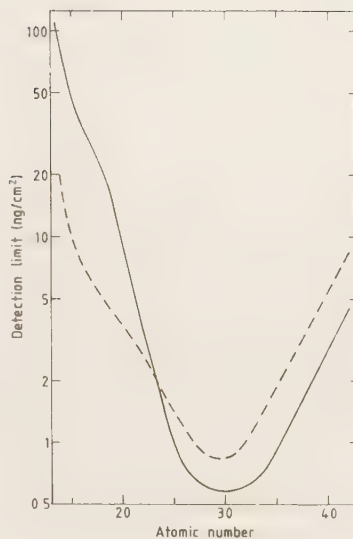
Table 2 Sampling and analysis conditions.

Filter/Backing	Flow rate\$ (l/min)	Exposed area (cm ²)	Irradiated area (cm ²)	Charge (μ C)	Current (nA)	Absorber (μ m)
Ghia	7.5	0.28	0.57	6	20	0
Millipore	2.0	8.76	0.57	30	100\$	340*
Nuclepore	1.7	0.71	0.25	20	80	340*
Polystyrene	1.0	<0.3	0.38	40	200	0

\$ flow rate through irradiated part of exposed area, * Mylar with 1.7% hole
\$ may cause losses of volatile elements

The Millipore and Nuclepore filters give a high count rate at low proton beam intensities due mainly to electron bremsstrahlung. Thus the beam intensity must be limited by the maximum count rate compatible with an undisturbed X-ray spectrum. However, the total transmission for different X-ray energies can be adjusted by inserting absorbers in front of the detector. This enables an optimization of the combination of maximum proton current that the sample can withstand and the maximum counting rate the electronics can handle. For our set-up we have chosen 2000 counts per second (cps) as maximum count rate. To obtain a more optimal detection limit profile for these type of filters a 340 μ m Mylar absorber with a 1.7% hole is inserted. Thus the intensity of the low energy X-rays - including electron bremsstrahlung - is reduced, allowing a more intense proton beam to be used which results in improved detection limits except for the lightest elements. In Fig 2 the detection limits for a 1 mg/cm² Nuclepore filter analysed with and without this external absorber and equal

Fig 2. Comparison of detection limits as a function of the atomic number obtained in equal irradiation time without any external absorber (dashed line) and with a 340 μm Mylar absorber with a 1.7 % hole (solid line). The analysing time was approximately 4 minutes in both cases while the charge and count rate were 6 μC and 2000 counts per second (cps) in the first case. In the second case these parameters were 20 μC and 400 cps respectively.

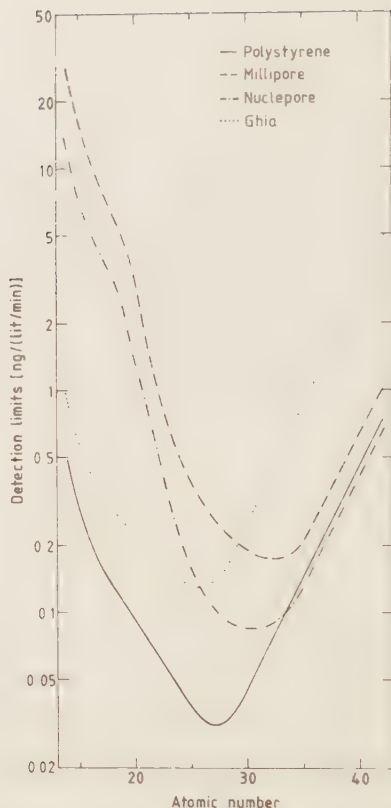


analysing time are compared. Most of the interesting lighter elements, which may be quantified by PIXE, are usually quite abundant in ambient aerosol samples making a loss in sensitivity for them quite acceptable.

The gamma-ray production in the fluorine, contained in the Ghia filters results in a very high count rate of signals with high energy, which cause peak broadening in the spectrum already at moderate count rates (1000 cps). We have therefore analysed these filters using a low beam intensity and no external absorber. Finally the thin polystyrene film does not require any external absorber although this film can withstand a high beam intensity.

The substrate detection limits normalized to the flow rate through the irradiated part of the exposed area are shown in Fig 3. These detection limits can be regarded as effective limits making inter-sampler detection limit comparisons meaningful. The very thin polystyrene film generally has the lowest detection limits. The Millipore filter has the highest detection limits for lighter elements while the Ghia filter has the highest detection limits for higher Z elements. The latter is due to the gamma-ray production in the teflon filter resulting in an increased high-energy background from gamma-rays scattered in the detector. Comparing the detection limits in Fig. 3 it must be taken into account that the accumulation mode aerosol particles are collected on at least 3 stages plus a bottom filter in the cascade impactor while in the

Fig 3. Detection limits in ng per litre per min of three filters and the impactor backing material polystyrene as function of the atomic number. The values are normalised to the flow rate of the irradiated part of the substrate (see table 2). It should be pointed out that for elements contained in the blank substrates the efficient detection limits may be considerably increased (see table 3).



two stage filter sampler the same mode is collected on one Nuclepore filter. Since the impactor bottom filter often consists of a Nuclepore filter used with a lower flow rate than in the two stage sampler, the cascade impactor added detection limits (assuming elements to be detected on all stages) are higher than those for the Nuclepore filter only.

In table 3 average blank contents and their variations, based on 7-10 blanks of each of the four substrates are given. In order to detect an aerosol concentration of a specific element the remaining concentration when the average blank content is subtracted should exceed three standard deviations (3σ) of the blank content as given in table 3. Impurities especially for the elements S, Cl, Ca and Fe, being quite variable, increase the detection limits considerably in some of the substrates. We have observed that the relative blank content variations are largest for the polystyrene films resulting in a 3σ always above the mean. The Millipore filters exhibit the smallest variations, 3σ often being in the 50-100% range of the mean.

Table 3 Average blank contents and three standard deviatons (in brackets) of the blank content, normalised to the flow rate through the irradiated part of the substrate. Unit ng per litre per min.

Substrate	Ghia	Millipore	Nuclepore	Polystyrene
Flow rate(l/min)	7.5	2.0	1.7	1.0
Element				
S	0.62(1.7)	12(15)	9.8(27)	3.8(7.3)
Cl	-	50(18)	-	9.3(16)
K	-	34(16)	-	-
Ca	0.31(1.1)	44(12)	2.3(2.9)	15(26)
Ti	0.24(0.64)	-	-	0.18(0.14)
Mn	-	0.53(0.48)	-	-
Fe	0.28(1.1)	1.6(0.62)	2.2(2.0)	0.43(0.37)
Ni	-	-	0.10(0.10)	0.44(0.40)
Cu	-	0.30(0.31)	-	0.12(0.090)
Zn	-	1.8(0.55)	-	0.90(0.27)
Sr	1.6(1.9)	-	-	0.37(0.26)

- below detection limit as given in Fig 3.

THICKNESS CORRECTIONS FOR UNIFORM SAMPLES

When exceeding an aerosol deposit thickness of some tenths of a mg/cm^2 corrections for X-ray self absorption and proton energy loss have to be made in order to obtain accurate results. Assuming urban and rural matrices as shown in table 4, elemental correction factors calculated for different uniform (rectangular) deposit thicknesses are plotted in Fig 4 and 5. The main differences discerned when comparing these figures, are the relatively higher corrections necessary for chlorine and to somewhat lesser extent K and Ca in the rural matrix, while the corrections for P and S are lower. The higher sulphur content in the latter matrix explains the first difference while the second difference can be explained by the higher silicon content in the urban matrix. The corrections for a certain thickness can be studied in more detail in Fig 6. Here it is evident that the sulphur K absorption edge strongly affects the X-ray absorption correction especially for chlorine. The total correction, proton energy loss correction and X-ray absorption correction as function of the atomic number for K_{α} X-rays can be studied in Fig 7. Two thicknesses of rural matrixes are plotted.

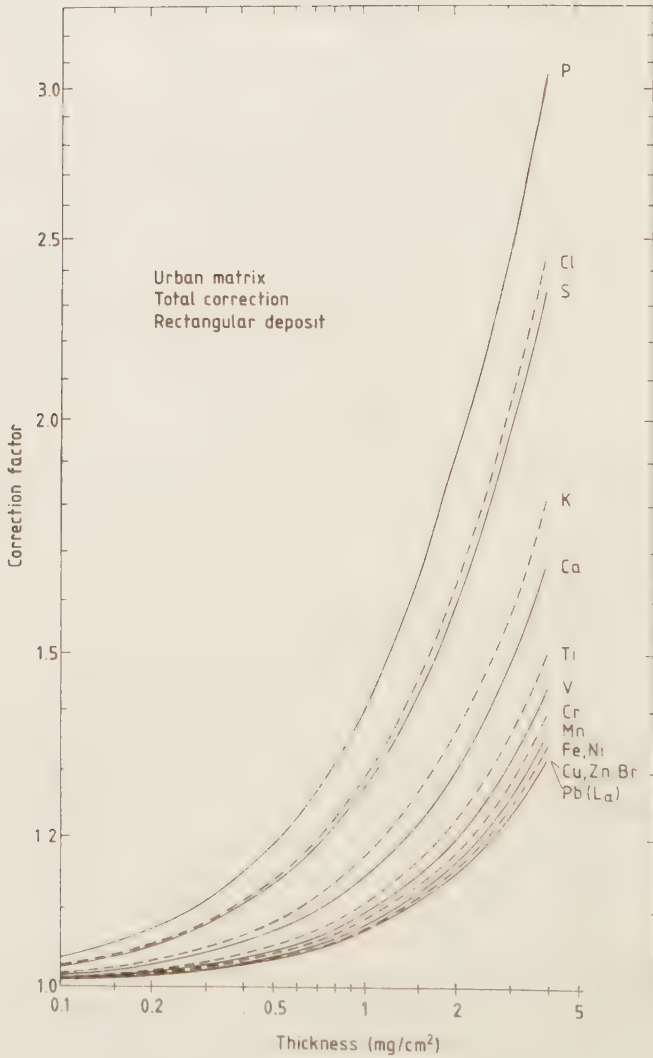


Fig 4. Urban matrix correction factor for different elements plotted as function of the sample thickness assuming uniform (rectangular) deposit. Both X-ray absorption and proton energy loss corrections are included in the correction factor.

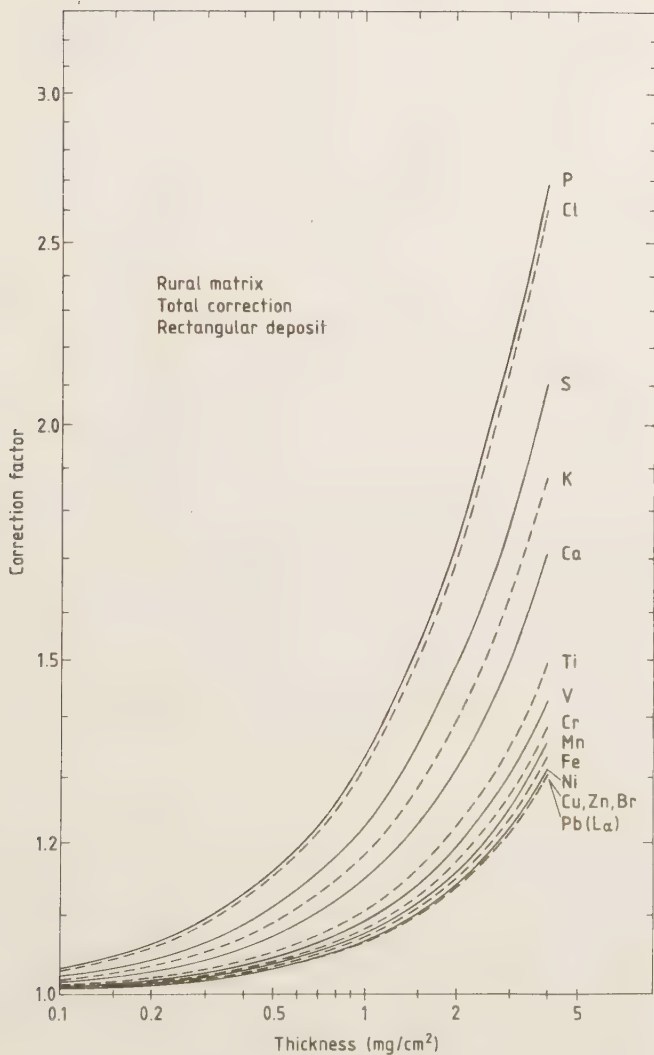


Fig 5. Rural matrix correction factor for different elements plotted as a function of the sample thickness assuming uniform (rectangular) deposit. Both X-ray absorption and proton energy loss corrections are included in the correction factor.

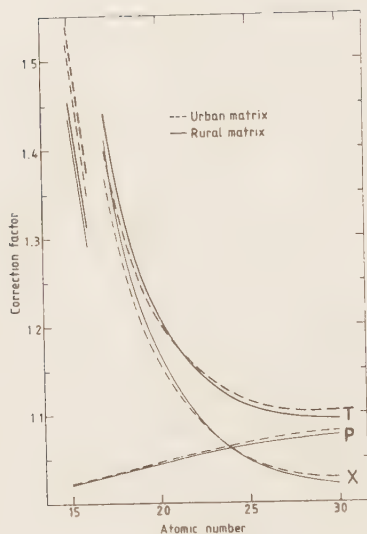


Fig 6. Comparison of urban and rural matrix total corrections (T), X-ray self absorption corrections (X) and proton energy loss corrections (P) for a 2.8 mg/cm^2 conical deposit as function of the atomic number. Corresponding rectangular deposits are approximately 1.3 mg/cm^2 thick.

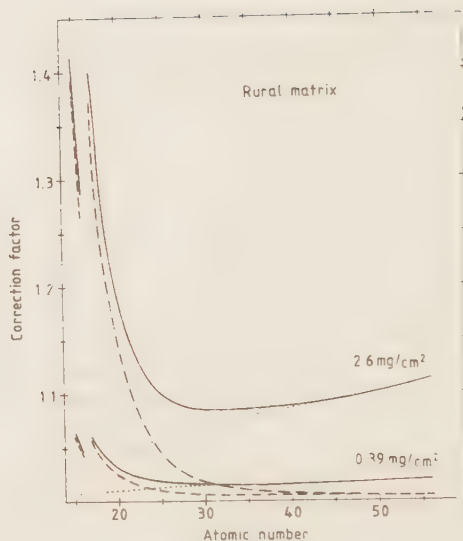


Fig 7. Total corrections (solid line) including X-ray absorption corrections (broken line) and proton energy loss corrections (dotted line) for a 2.6 and a 0.39 mg/cm^2 conical rural matrix deposit as a function of the atomic number. Corresponding thicknesses for rectangular deposits are approximately 1.2 and 0.20 mg/cm^2 , respectively.

The thickness corrections are calculated using X-ray absorption data from Veigle (1973) and proton stopping data from Northcliffe and Schilling (1970). The sample deposit has thus been divided into at least 50 layers in which constant proton energy is assumed. The relative decrease of the X-ray cross section from the surface to each layer and the X-ray self absorption from each layer are weighted and summed over all layers to give a correction factor. X-ray production cross sections are calculated from the measurements and fit given by Akselsson and Johansson (1974).

Table 4 Urban and rural accumulation mode aerosol composition in %.

Element	Urban*	Rural**
H	4.6	2.9
C	40	25
N	3.5	13
O	32	40
Na	1.0	1.5
Mg	0.7	0.3
Al	1.3	0.8
Si	3.4	-
S	5.6	13
Cl	0.7	1.0
K	0.8	0.7
Ca	1.4	0.7
Fe	2.2	0.5
Zn	1.0	0.3
Pb	2.2	0.5

* adopted from Rahn (1976) subtracting 60-70% of the crustal and marine components (Na, Mg, Al, Si, Cl, K, Ca, Ti and Fe) and adding oxygen proportionally from assumptions of the most likely oxide components of the elements.

** adopted from measurements at rural locations in southern Sweden.

THICKNESS CORRECTIONS FOR NON-UNIFORM SAMPLES

The shape and thickness of the samples collected by the cascade impactor have been studied both in an optical microscope and with a special technique where the transmission of a 0.2 mm diameter X-ray beam (e.g. Ag L X-rays) through different parts of the sample is measured. The latter technique is illustrated in Fig 8 and further described by Carlsson et al (1981). The measurements showed that the sample deposit could be approximated by a cone with a large base to height ratio. A computer code was developed to calculate the thickness corrections for a conical sample deposit. A cone was thus divided into 30 conical layers in which constant proton energy is assumed. In Fig 9 some geometric variables involved in these calculations are shown. Taking an arbitrary volume element with distance r and projected angle ν relative to a cone layer top, it can be seen that the X-ray path out of the volume element can be calculated from geometric relations in the r , ν , θ and φ variables. The proton path length to reach a certain cone layer is constant. The X-ray

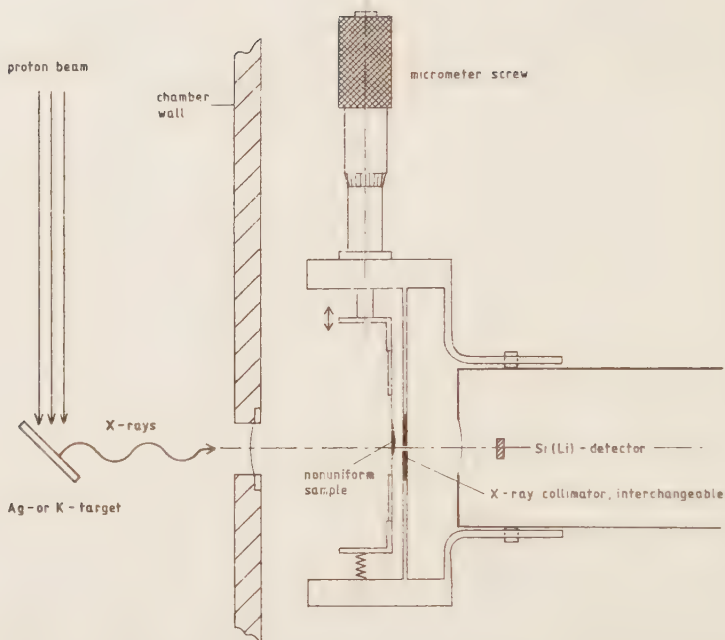


Fig 8. Principle of Ag(L) X-ray attenuation measurements for impactor samples. (From Carlsson et al (1981).)

contribution from each volume element can be summed and thus the total correction factor for a given sample thickness may be obtained.

The elemental correction factors for conical samples have approximately the same curvature as in Figs 4 and 5 if the sample thickness scale is changed. For cone peak thicknesses smaller than about 1 mg/cm^2 a correction factor corresponding to a rectangular deposit thickness multiplied by a factor of 0.50-0.48 will apply. For cone peak thicknesses from 1-3 and 3-9 mg/cm^2 the factor required to multiply a rectangular deposit thickness giving the same correction will be 0.48-0.46 and 0.46-0.43 respectively.

To ensure good analytical accuracy every impactor sample thicker than a few tenths of mg/cm^2 should be measured as described earlier. In practice this would be very time consuming. Therefore four sets of impactor samples with very low, low, intermediate and high loading representing an urban and a rural matrix, respectively, were selected and characterised as described earlier. By visual inspection all impactor samples are classified into one of these four

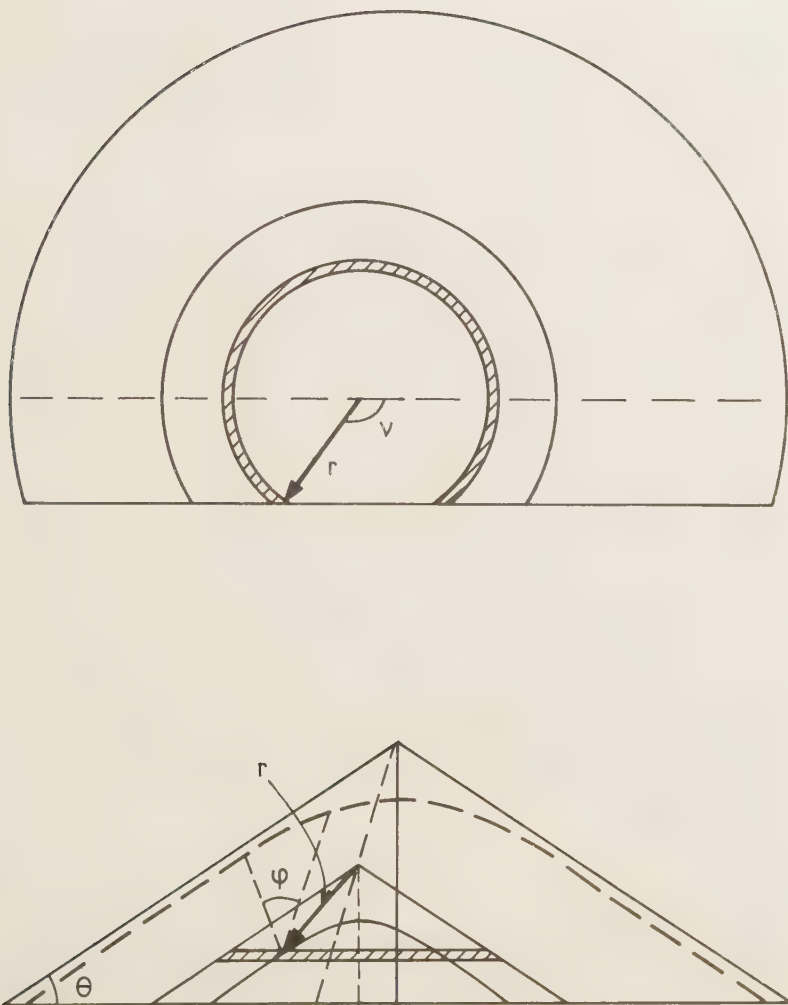


Fig 9. Diagrammatic representation of a cone formed sample where the important variables for the thickness factor calculations are shown. ν is the angle between the diameter in the plane of the proton and X-ray paths and the projection of r (the distance from the cone layer top to an arbitrary volume element) on the plane of the cone base. ϕ is the angle between the proton path and the X-ray path.

classes and corrections applied. Naturally this is a somewhat uncertain procedure but the errors are thus changed from a large systematic underrepresentation to a rather large but less systematic error. The largest error to occur corresponds to the difference between an intermediate and a high loading correction, which is about 40% for Cl and 15% for Fe. Furthermore when reaching deposit thicknesses on the 5 to 10 mg/cm² level, interstage and wall losses have been observed. This means that the impactor is overloaded and is no longer working according to theory.

In recent years the accumulation mode matrix has been more thoroughly investigated e.g. Countess et al (1980), Dzubay (1980), Heintzenberg et al (1981) and Stevens et al (1980). The referenced data comprise aerosol measurements in Northern Europe (the rural matrix assumed in this paper), in the Arctic and in rural and urban U.S.A. all having 16-18% of the accumulation mode mass in elements that can be quantified by PIXE. Using this very constant relative amount, elements not measured can be added proportionally according to an assumed matrix. The total sample thickness can thus be obtained and corrections applied. If large corrections are experienced this procedure should be iterative. Comparing the urban and rural matrices used in this work (table 4) sulphur and silicon are found to exhibit variations of significance for the correction factor calculations (compare Fig 4 and 5). Therefore we suggest that separate aerosol matrices are used for urban and rural measurements. This correction procedure is of course also applicable to uniform samples. Furthermore it is more reliable than the one described earlier unless very special aerosol compositions are experienced e.g. close to a dominating source. However, the matrices consist mainly of carbon and oxygen which make the correction factors rather insensitive to variations of the relative light element composition.

SAMPLING OPTIMIZATION

Dependent on the aims of an aerosol composition study basically three factors affect the sampler choice. These factors are related to the demands on time resolution, elemental information and size distribution. Only the first two factors will be further considered here. Interpretations of particle size distributions with respect to production mechanism, giving information on source type, have been made by Willeke and Whitby (1975). van Grieken et al (1976) have evaluated the cascade impactor performance and compared this with geophysical causes of elemental size distribution differences. The toxicity

of the urban aerosol with respect to its size distribution has been discussed by e.g. Natusch and Wallace (1974). The particle size distribution also has an important influence on the radiation balance as discussed by Jaenicke (1980).

In order to compare the samplers (substrates) with respect to obtainable time resolutions in different environments, assumptions of concentration levels representative of urban, rural and remote locations are made (see table 5). A conservative approach is then taken requiring the detection limit concentrations to be 10 times below the typical concentrations in the different environments as given in table 5. This approach ensures detected concentrations in practically all samples since often the maximum variation in elemental concentrations is less than $\pm$ one order of magnitude.

Table 5 Assumed urban, rural and remote accumulation mode aerosol compositions. The marine component, calculated from bulk sea composition using Cl as tracer, has been subtracted from the S, K, Ca and Br concentrations. Unit ng/m^3 .

	Urban*	Rural§	Remote^
S	4.000	800	100
Cl	500	60	200
K	600	40	3
Ca	1.000	40	3
Ti	80	2	0.2
V	60	2	0.05
Cr	20	2	0.05
Mn	100	3	0.05
Fe	1.500	30	1
Ni	20	1	0.05
Cu	200	2	0.05
Zn	700	20	0.2
Br	300	3	0.02
Pb	1.600	30	0.2

* Average matrix from Rahn (1976), recalculated as described in table 4.

§ Southern Sweden (inland site).

^ Arctic summer (marine site).

Bearing in mind that the data evaluation often includes relating the aerosol composition to different sources, some of the elements have been classified into source representative groups. S, V and Ni are thus assigned to represent fossil fuel combustion and Br (non-marine) and Pb to indicate leaded petrol

combustion. Cr, Cu and Zn, although having different sources, are used to represent general industrial activities. Since our discussions are confined to the accumulation mode aerosol composition Ti, Mn and Fe, having anthropogenic high temperature sources, cannot be included in the latter group because coarse mode concentrations (usually erosion products) would probably also influence the accumulation mode concentrations. In Table 6 the calculated minimum sampling times for detecting one element in each of the three source representative groups are given. Minimum sampling times needed to detect both sulphur and certain heavy metals (Ti, V, Mn, Fe, Ni, Cu, Zn and Pb) are also listed.

Table 6 Calculated sampling times (hours) needed to detect concentrations (one tenth of those given in table 5) for the best detectable element in each source representative element group. The sampling times necessary to detect both sulphur and all the heavy metals measured are also given. The sampling times given for the cascade impactor represent the longest time required by the polystyrene film or the Nuclepore filter (sampling and analysis as in table 2 but normalized to 1 l/min) assuming the accumulation mode aerosol concentrations to be evenly distributed on the three polystyrene coated stages and the Nuclepore bottom filter stage.

Urban aerosol composition	GHIA Total filters	Millipore	Nuclepore second stage	Polystyrene or Nuclepore
Fossil fuel combustion	0.071(S)	0.63(S)	0.83(Ni)	6.4(V)
Traffic	0.18(Pb)	0.059(Pb)	0.033(Pb)	0.23(Pb)
General industrial activities	0.060(Zn)	0.13(Zn)	0.021(Zn)	0.26(Zn)
Sulphur and heavy metals§	1.3(Ni)	4.3(Cr)	1.8(Cr)	13(Ni)

Rural aerosol composition

Fossil fuel combustion	0.35(S)	3.1(S)	5.6(S)	38(S)
Traffic	9.4(Pb)	3.2(Pb)	1.8(Pb)	12(Pb)
General industrial activities	2.1(Zn)	6.0(Zn)	0.75(Zn)	9.0(Zn)
Sulphur and heavy metals§	53(Ti)	92(Ti)	44(Ti)	300(Ti)

Remote aerosol composition

Fossil fuel combustion	2.8(S)	25(S)	45(S)	300(S)
Traffic	1400(Pb)	480(Pb)	270(Pb)	1800(Pb)
General industrial activities	210(Zn)	460(Zn)	75(Zn)	900(Zn)
Sulphur and heavy metals§	1400(Pb)	2500(V)	1100(V)	7700(V)

§ Ti, V, Mn, Fe, Ni, Cu, Zn and Pb

Urban sampling with a time resolution of less than one hour gives information on at least one element in each source group for all samplers but the cascade impactor. However, if information on the eight heavy metals is required the sampling time must be increased. In both rural and remote environments the Nuclepore two stage filter sampler would allow the shortest sampling time, being of the order of six hours and two weeks, respectively when detecting at least one source representative element in each of the three groups. Simultaneous information on both sulphur and the eight heavy metals would require sampling times of 4 days and 1.5 months in rural and remote environments, respectively. More detailed size distribution information as achieved by the cascade impactor, requires a factor of five or more increase in sampling time. If sulphur is the only element of interest a sampler fitted with Ghia filters results in the shortest sampling time being a factor of ten shorter than for the other samplers.

The sampling times required to obtain information about certain elements in certain environments should also be considered with respect to sample thickness and possible corrections. In table 7 sampling times resulting in deposit thicknesses requiring a significant correction for the lightest elements measured are given. The remote sampling times have been calculated from the rural aerosol matrix which make them somewhat more uncertain. A remote matrix (presently not available) would probably contain relatively more sulphate and somewhat less metals and carbon (i.e. the primary aerosol constituents).

Table 7 Calculated sampling times (hours) needed to obtain a sample thickness of 0.5 mg/cm^2 for uniform deposits and 1.0 mg/cm^2 (peak) for a non-uniform deposit (0.5 mm base-diameter cone) which require 10-20% corrections for the lighter elements (i.e. P, S and Cl). Concentrations of ten times those given in table 5 were assumed when calculating the sampling times.

Environment	Ghia	Millipore	Nuclepore	Polystyrene
Urban	0.44	3.3	1.7	0.061
Rural	5.1	39	20	0.71
Remote*	40	310	160	5.7

* calculated from the rural matrix.

When comparing tables 6 and 7 it should be remembered that the sampling times in table 6 make possible the detection of concentrations 10 times below the average concentrations. Sampling times in table 7 assume aerosol concentrations 10 times higher than the average concentrations as given in table 5. Thus the elemental concentrations used in these tables differ by two

orders of magnitude which represents the "worst case" variations to be found in the atmosphere.

Generally the filter samplers (Ghia, Millipore and Nuclepore) are least critical with respect to the sampling time. In all three environments information about at least sulphur and some of the metals can be obtained in a sampling time not resulting in deposits requiring thickness corrections. The cascade impactor however, must be operated with great care in order that too thick samples are not obtained which are beyond the impactor theory. Corrections have to be applied, at least for some of the stages in all environments if information on the source representative elements is to be obtained. For most of the elements the impactor bottom filter has much higher detection limits than the polystyrene film, requiring the longest sampling times. On the other hand the conical deposits on the polystyrene films are the first to reach levels where thickness corrections become necessary. With the sacrifice of some elements on the bottom filter the impactor could be operated with sampling times a factor of five shorter than given in table 6, requiring smaller corrections.

SUMMARY AND CONCLUSIONS

PIXE-analysis and properly designed low volume aerosol samplers constitute very powerful tools in ambient aerosol studies. In order to obtain accurate results some care must be taken not to have too thick samples which is a problem especially when dealing with inhomogenous samples. In an ambient aerosol matrix elements lighter than chromium are primarily affected by X-ray absorption effects which are in the 10 - 20% range at a 0.5 mg/cm^2 uniform thickness for P, S and Cl. Proton loss correction is most evident for heavier elements and reaches the 10% level at a uniform thickness of approximately 1.5 mg/cm^2 for elements with atomic number 30 - 50. Applied to conical deposits these thicknesses should approximately be doubled.

The calculated sampling times based on certain realistic assumptions concerning exposed area, flow rate and analytical parameters, were mainly of the same order of magnitude for the combinations of samplers and substrates compared. However, in most cases the Nuclepore two stage filter sampler proved to have the shortest sampling time (only the accumulation mode fraction considered). In order to always obtain information on elements representative of fossil fuel combustion (S, V or Ni), leaded petrol combustion (Br or Pb)

and general industrial activities (Cr, Cu or Zn) the detection limits should be a factor of ten lower than the average elemental concentrations. In urban, rural and remote atmospheres this would require sampling times of half an hour, six hours and two weeks respectively. The urban time resolution would thus be sufficient for interpretations of short time aerosol concentration fluctuations associated with e.g. traffic intensity variations. Furthermore the urban and the rural time resolutions allow day/night and synoptical meteorological variations to be resolved. The remote time resolution of two weeks can be used to study seasonal or yearly concentration trends. However, when discussing required sampling times the obtained deposit thicknesses and their need for corrections must also be considered. The sampling times required to obtain sufficient information at concentrations 10 times below the average levels often are of the same magnitude or larger than sampling times producing a deposit where corrections are necessary assuming concentrations 10 times above the average levels. The combination with an instrument capable of continuously measuring the accumulation mode aerosol mass (e.g. an integrating nephelometer (Charlson et al 1974) or a two stage beta radiation mass monitor (Macias and Husar 1976)) and controlling the sampling time would thus be very useful.

The detection limits obtained can be improved by increasing the irradiation time, by using pumps capable of creating even higher flow rates or by using thinner, cleaner and more porous filters. Of course the electronics of the analytical system can be improved allowing e.g. higher count rates, resulting in lower detection limits. To study only those samples having concentrations e.g. above the average concentrations is another approach to obtain shorter sampling times. The analytical conditions, the choice of sampler (substrate) and sampling time should therefore be intimately related to the aims of a project.

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Paper II

BACKGROUND AEROSOL COMPOSITION IN SOUTHERN SWEDEN - 14 micro and macro constituents measured in seven particle size intervals at one site during one year

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ABSTRACT

The aerosol composition as a function of particle size, has been studied at a rural location in southern Sweden, during a period of one year. The sulphur and heavy metal concentrations have been measured in 113 cascade impactor samples by particle induced X-ray emission (PIXE). Elemental concentrations were one to two orders of magnitude lower than in central Europe but only a factor of 2 - 4 higher than the winter concentrations in the Arctic. The size distributions were rather broad except for some of the anthropogenic components. Enrichment factors calculated in both the fine and coarse particle mode gave information on possible anthropogenic contributions in the fine mode for the expected soil derived elements K and Mn. The samples were classified according to calculated air mass trajectories. Air masses having traversed the British Isles or central Europe contained up to an order of magnitude higher concentrations of known anthropogenic components e.g. S, V, Ni, Cu, Zn and Pb than air masses originating in the north Atlantic. The foreign contribution of the elemental concentrations was estimated to 70-80% for S and Pb, 50% for Ni and 30% for V. The anthropogenic components (except sulphur) showed the largest seasonal variations being highest in the winter. Dry deposition estimates indicate that the wet deposition was dominant for the fine particle oriented elements (S, V, Ni, Cu, Zn and Pb), while for the large particle oriented elements oriented Ti and Fe dry and wet deposition were of equal importance.

An appendix concludes this paper and presents elemental concentration frequency distributions in the fine and coarse mode.

INTRODUCTION

Aerosol studies using the PIXE-analysis technique in combination with suitable sampling devices such as filter, streaker or cascade impactor samplers present great opportunities for large scale aerosol composition measurements. This study includes 113 sets of samples taken with a 7-stage cascade impactor, giving information on 10-20 elements (of which 14 are presented here) on each stage which results in approximately 11 000 data points. In this paper we intend to give an overview of the large data set. We will therefore concentrate on a discussion of the results in terms of yearly and seasonal elemental concentration averages as well as averages calculated according to the history of the air mass. A discussion of the calculated contribution from Swedish and Finnish sources, the average enrichment factors and the dry deposition is also included. In an appendix the frequency distributions of the elemental concentrations in the coarse and fine particle mode are shown.

Measurements of trace element concentrations in different particle size fractions of the atmospheric aerosol at rural and remote locations (some hundred to several thousand kilometers from major source areas) have not been carried out very extensively. Rahn (1971) reported data from Canada on elemental composition in five particle size fractions. Size-segregated samples from rural locations in Great Britain were obtained during many years and analysed for several trace metals (e.g. Cawse 1974). Flocchini et al. (1976) studied particle size distribution and elemental composition of California's aerosol at thirteen urban and non-urban sampling sites. Johansson et al. (1976) obtained cascade impactor samples from a number of coastal and inland stations in Florida. The relation between sulphur concentration and other trace elements in South America was determined by Lawson and Winchester (1978). Crustal reference elements in non-urban aerosols were studied as a function of particle size by Lawson and Winchester (1979). All these studies except Rahn's and the U.K. measurements were based on the PIXE analysis technique although the sampling methods were different.

The long range transport of some man-made air pollutants is now of common and widespread interest. Publications by Bolin (1971), Brosset and Åkerström (1972), Rodhe et al. (1972), Bolin and Persson (1975), Brosset (1976) and the OECD/LRTAP study 1973 - 1974 (OECD 1977) have lead to a general recognition of long-range transport with particular emphasis on sulphur. Much less is known about the long-range transport of micro components, typical concentrations in rural locations and amounts deposited in e.g. Sweden. Systematic moss analysis

(e.g. Rühling and Skärby 1979) give valuable qualitative information. Some measurements of aerosol trace metal concentrations at rural locations in Scandinavia have been performed (e.g. Semb 1979, Heintzenberg et al 1979; see also Laveskog and Thorsmark 1979). However, the study presented here is probably the most extensive so far in this area.

EXPERIMENTAL

The sampling site (Sjöängen) is located between Lake Vänern and Lake Vättern (fig. 1) within a representative basin for the Swedish programme within the International Hydrological Decade. It is also the site for regular meteorological and atmospheric chemistry measurements, some of them part of a national Swedish programme for the supervision of environmental quality. The area is described in more detail in Hydrological data-norden (1976). The nearest city is at a distance of about 30 kilometers. Larger cities (>100000 inhabitants) and areas with many industries are found some 200 kilometers from the site (see fig. 1), except for one smelter which is 110 kilometers southwest of the sampling site. The distance to the nearest agricultural field is about 1 kilometer while larger farming areas are more than 10 kilometers away. There is a small road nearby having a very low traffic intensity (<10 vehicles/day). Parallel measurements at this site and another site at three kilometers distance, with two nephelometers during several months, indicate that the site is practically free from local contribution to aerosol volume in accumulation mode.

The sampling device was placed on top of a tower 17 meters above the ground, in an area which is cleared from trees and mainly covered with grass. The sampler is a cascade impactor of Batelle design (Mitchell and Pilcher 1959) with a flow rate of 1 l/min and with the following size fractions given for aerodynamic diameter (of unit density): <0.25, 0.25-0.5, 0.5-1, 1-2, 2-4, 4-8, >8 μm . The stage collecting particles less than 0.25 μm consists of a 0.4 μm pore diameter Nuclepore filter having an efficiency (at 50% vacuum) estimated to be better than 80% for all particle sizes. Bounce-off was kept low by using a paraffin coating on the impaction surface (Lawson 1980) and avoiding high loading of sample material. The large particle intake efficiency of the impactor and cover varies with the wind speed and the first stage (>8 μm) was consequently only used to give an upper particle size limit. The material found on this stage was not further evaluated and therefore 'total' concentrations in the following are referring to concentrations on particles

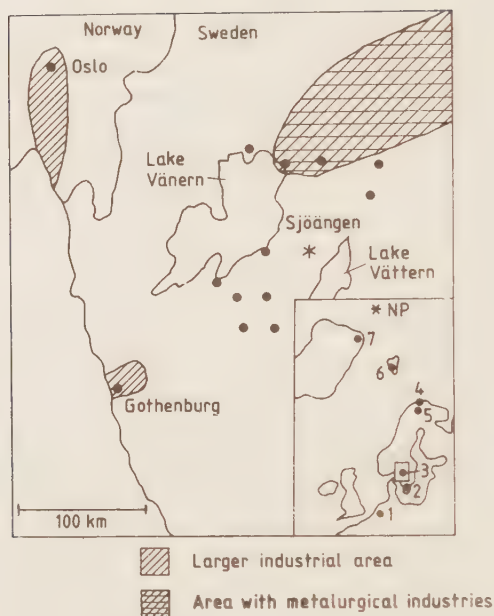


Fig 1. Map showing the location of the sampling site (Sjöängen), some major cities (Gothenburg and Oslo with several hundred thousand inhabitants) and the nearest cities (having up to 100 000 inhabitants). Major industrial areas are indicated. The referenced sampling locations in table 2 are also pointed out.

less than $8\text{ }\mu\text{m}$ diameter. It should be noted that at high wind velocities the intake efficiency for particles finer than $8\text{ }\mu\text{m}$ might also be affected. However, the large particle intake efficiency can be increased by employing a turbulence inducing sampling hood (in this study a conical hood was used). This was found by Pattenden and Wiffen (1977) in laboratory experiments and by May et al (1976) in a field experiment. Furthermore Benarie (1977) has compared a low and a high volume sampler (the latter often expected to have a higher intake efficiency) with rather similar sampling heads in an urban and a laboratory study. In the latter study silica dust with aerodynamic diameters in the $2 - 50\text{ }\mu\text{m}$ range were used. No significant concentration differences between the two samplers were found. Based on these studies we believe that the loss in the particle intervals below $8\text{ }\mu\text{m}$ are not of such a magnitude that they would affect the conclusions drawn in this paper.

Samples were taken every third day during a one-year-period. The sampling time, 24 hours, is usually long enough to provide sufficient material for a satisfactory analysis and short enough to permit a detailed interpretation

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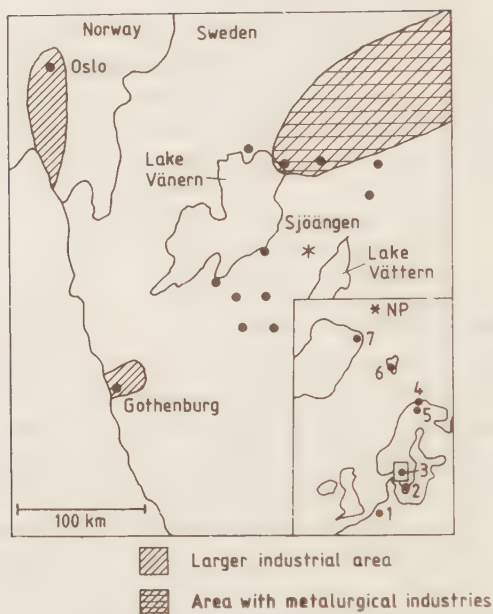


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with regard to meteorology and long-range transport. Elemental analyses were made by particle induced X-ray emission (PIXE; Johansson et al. 1975). Samples collected during the first five months of the project were analyzed using beams of 2 and 3 MeV protons generated by the Van de Graaff accelerator at the Niels Bohr institute in Copenhagen, Denmark. The remaining samples were analysed using a beam of 2.5 MeV protons from the Pelletron accelerator at the Department of Nuclear Physics, Lund Institute of Technology, Lund, Sweden. The radiation time was approximately 3 minutes per sample. Spectra were evaluated using a computer code developed by Kemp (in Copenhagen) and by Kaufmann (in Lund; Kaufmann et al. 1977). The accuracy and precision of the PIXE analysis is usually 10-15 percent. For a limited number of samples which were slightly overloaded the uncertainty, however, is higher because of corrections for the X-ray absorption and losses in the impactor. The reproducibility of the sampling is about 15% (van Grieken et al. 1976). The overall uncertainty (one standard deviation) in most of the individual concentration estimates is therefore of the order of 25% or less which is low compared to the observed day-to-day variations in elemental concentrations.

DATA PRESENTATION AND INTERPRETATION

Elemental concentrations and their variability

We start the presentation with a statistical summary of the concentration distribution for the fine or accumulation ($<1 \mu\text{m}$) and coarse ($1-8 \mu\text{m}$) particle modes (table 1 and appendix). Attempts have been made to fit a bimodal log-normal size distribution to individual elemental concentration particle size distributions using non-linear regression (Hansson and Lannefors 1980). The impactor cut-off characteristics were thus taken into account. This procedure gave consistent results for stage-wise sums of the elements but was not successful for individual elements. The division between the fine and coarse particle mode made in table 1 is one of many possible ones. In a following section the size distribution will be studied in more detail.

The frequency distribution of elemental concentrations (shown in the appendix) can not be described with a simple mathematical expression valid for several components although some elements show a tendency to a log-normal distribution. We have therefore chosen to present both medians and arithmetic means since both of them have their special merits. The variability is shown by quartiles. The wide range in concentration is apparent - 75% of the cases

are roughly between 1/4 and 4 times the median value and more than 2 orders of magnitude between the few highest and the few lowest values for most components both in the fine and coarse particle modes.

Table 1. Statistical summary of elemental concentrations at Sjöängen based on 113 sets of 24 h measurements during one year. T, F and C refer to particle size intervals of <8, <1 and 1-8 μm respectively. The values are given in ng/m^3 .

	Arithmetic			Lower			Median			Upper		
	mean			quartile						quartile		
	T	F	C	T	F	C	T	F	C	T	F	C
S	800	(680,110)		240	(190,32)		480	(390,83)		1100	(920,130)	
Cl	190	(25,160)		18	(<4.5,7.6)		55	(12,32)		190	(27,180)	
K	76	(46,30)		35	(17,13)		50	(32,22)		100	(60,39)	
Ca	74	(18,56)		28	(6.7,18)		59	(12,42)		110	(22,73)	
Ti	5.0	(1.4,3.6)		1.6	(0.52,0.93)		3.4	(0.87,2.3)		7.0	(1.7,5.1)	
V	2.5	(2.1,0.38)		0.68	(0.61,<0.060)		1.5	(1.4,0.19)		3.9	(3.1,0.63)	
Cr	2.8	(1.9,0.83)		1.2	(<1.0,0.13)		2.0	(1.4,0.47)		2.9	(1.9,1.1)	
Mn	6.7	(3.9,2.8)		2.5	(1.1,0.85)		4.5	(2.6,1.7)		9.5	(5.2,3.8)	
Fe	88	(34,53)		3.0	(9.5,15)		48	(18,29)		140	(55,70)	
Ni	1.5	(1.2,0.36)		0.60	(0.44,<0.060)		1.1	(0.84,0.22)		2.1	(1.6,0.45)	
Cu	2.4	(1.8,0.54)		0.59	(0.40,<0.075)		1.1	(0.79,0.23)		2.8	(2.2,0.59)	
Zn	24	(16,7.5)		5.0	(3.9,<0.24)		15	(10,3.0)		37	(26,10)	
Br	2.8	(2.0,0.71*)		0.85	(<0.55,<0.30)		2.4	(1.8,<0.30)		3.8	(2.8,0.88)	
Pb	21	(17,4.0)		6.8	(5.6,<0.75)		12	(11,2.1)		32	(26,5.5)	

* more than 50% of the values below the detection limit.

The amount of material collected is sometimes too small for reliable analysis. When this is the case, a concentration half the value of the detection limit is assigned to the sample (detection limit here taken to be three times the square root of the X-ray background or half the filter blank whichever is the greatest). For some elements this occurs quite frequently at some impactor stages. It should be noted that if a geometric mean value is calculated in these cases, it is heavily dependent on the assigned value.

Comparison between concentration at Sjöängen and at some other locations

In a scale of air pollution ranging from the European continent to the Arctic (see table 2) we find the concentration levels at Sjöängen to fit well. Concentrations of all components except sulphur and nickel are between one and

Table 2. One year average concentration at Sjöängen compared to elemental concentrations measured at some other selected sites (see figure 1). Unit ng/m^3 .

	Maassluis ¹⁾	Boalt ²⁾	Sjöängen ³⁾	Lakselv ⁴⁾	Jergul ⁵⁾	Ny-Ålesund ⁶⁾	Northern ⁷⁾
	Holland	southern Sweden	this work	northern Norway	northern Norway	Spitsbergen (winter)	Greenland (summer)
degrN	52	56	59	70	69	79	82
S	3700	1600	800	-	720	690	27
Cl	1500	1000	190	290	-	-	10
K	850	160	76	48	-	32	3.8
Ca	-	150	74	46	-	73	9.1
Ti	-	12	5.0	3.1	-	5.2	0.85
V	48	4.5	2.5	1.7	1.5	-	0.12
Cr	20	-	2.8	0.62	-	2.6	0.09
Mn	83	8.4	6.7	2.5	1.5	1.5	0.21
Fe	2100	110	88	51	-	64	6.4
Ni	0.2	2.7	1.5	1.3	-	0.7	0.08
Cu	200	4.6	2.4	2.3	-	1.9	-
Zn	420	24*	24	8.9	6.0	3.2	0.18
Br	160	-	2.8	4.7	-	-	0.29
Pb	-	32	21	5.5	6.4	4.9	0.20

* based only on measurements during one winter month

- 1) One day samples (18) taken during one year (Evendijk 1974)
- 2) Weekly samples taken during 3 summer months and 1 winter month (Wiman and Lannefors unpublished work)
- 3) 24-hour measurements every third day during one year (this work)
- 4) Weekly samples taken during one year (Rahn, personal communication)
- 5) Two-day samples taken continuously during one year (Hanssen et al 1980)
- 6) Two to five day samples taken continuously during 3 late winter weeks (Heintzenberg et al 1981)
- 7) Two to seven day samples taken during 2 summer months at Kap Harald Moltke (Flyger and Heidam 1978)

two orders of magnitude higher in Holland. On the other hand late winter concentrations at Spitsbergen (typical for the Arctic winter) and yearly mean concentrations at Jergul and Lakselv (northern Norway) are typically a factor of 2 - 4 lower than at Sjöängen. Arctic summer values (Greenland) are even lower. Distances to major source areas range in these cases from 1000 (Sjöängen), 2000 (N. Norway) to 3000-4000 kilometers (Spitsbergen and Greenland). Sulphur has the smallest relative difference in concentration when comparing sampling sites close to major source areas with those furthest away while some primary aerosol constituents most probably of anthropogenic origin (e.g. Zn and Pb) show a more rapid decrease with distance. Some components primarily of crustal origin like Ti show only a small variation between the sites except for conditions in Holland.

Distribution of elements in particle size intervals

Arithmetic average concentrations were calculated for each element in each of the seven particle size intervals and the result is given as a graphical display in figure 2. The distribution below 0.25 μm is unknown and we have for convenience assigned a lower limit of 0.06 μm . The size of the area below 0.25 μm is thus based on measurements although its shape is unknown. The mass median diameter is below 0.5 μm for V and Cu, between 0.5 and 1 μm , in increasing order, for Ni, Pb, S, Mn, Zn and K and between 2 and 4 μm for Cl, Fe, Ti and Ca. In fact, more than three quarter of the mass is found in particles less than 1 μm for the first 5 elements while for Mn and Zn the corresponding limit is about 2 μm . The elements Cl, Ca, Ti and Fe have on the other hand about three fourths of the mass in particles larger than 1 μm . One can, in fact, regard size distribution of several components as a combination of typical spectra for fine and coarse particle oriented components. This is especially obvious in the case of K but also for instance for Fe. The size distributions for Cr and Br are not included since detected concentrations normally only occur on one or two stages. It should be remembered that only particles with an equivalent aerodynamic diameter less than 8 μm are included in these calculations.

These size distributions are in line with previous findings and possible source processes such as combustion, soil erosion and seaspray and will be further discussed in a following section.

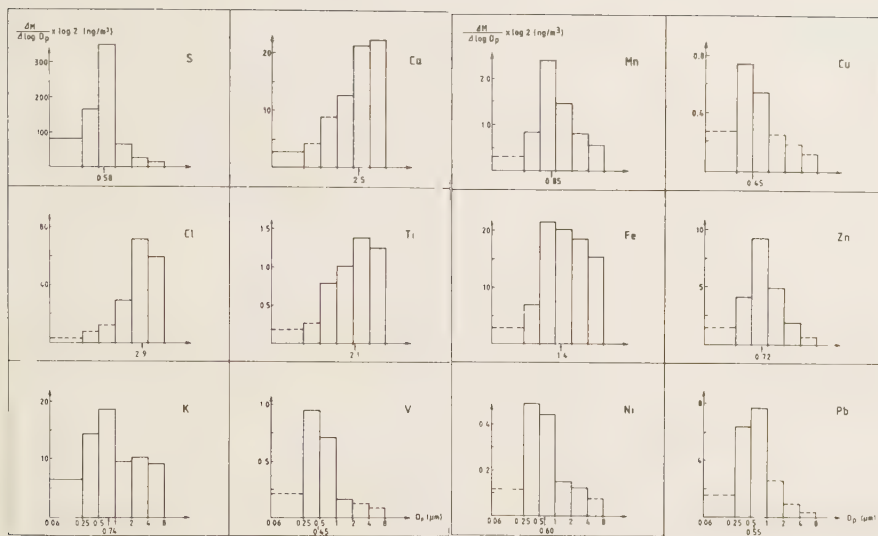


Fig 2. Particle size distributions of the elemental concentrations. The diagrams show the average concentration per logarithmic particle size interval versus the logarithm of the diameter. The numbers given on the ordinate are actual concentrations except for the $0.06 - 0.25 \mu\text{m}$ interval where the actual concentrations are obtained by multiplying the ordinate concentrations by 2. The numbers by the arrows are the mass median diameters (equivalent aerodynamic diameter in μm) for each element.

Enrichment factors

Enrichment factors have been used rather extensively to indicate which elements have sources in addition to natural ones (mainly sea-spray and soil erosion). Fractionation effects have been found to alter the relative composition of elements from that in the bulk material (e.g. Rahn 1976, Lawson and Winchester 1979 and Garland 1981). Used with caution the concept may still be useful and enrichment factors with titanium as reference element are given in table 3. The use of particle size fractionating samplers in combination with sensitive analytical techniques have enabled the interpretation of source types from elemental size distributions. Assumptions that anthropogenic emissions are mainly found in the accumulation mode while natural emissions are mainly found in the coarse mode have thus been made. The average enrichment factors are calculated according to:

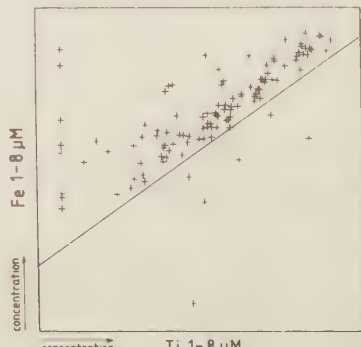
$$E = \frac{1}{113} \sum_{i=1}^{113} \frac{X(\text{aerosol})/Ti(\text{aerosol})}{X(\text{soil})/Ti(\text{soil})}$$

Table 3. Average enrichment factors in the fine and coarse modes and for the total concentrations, calculated using the average soil composition given by Bowen (1966).

	Fine(<1 μm)	Coarse(1-8 μm)	Total(<8 μm)
S		480	1400
Cl		12000	5200
K	16	6.2	8.3
Ca	6.0	11	7.4
Ti	1.0	1.0	1.0
V		11	36
Cr		30	54
Mn	19	8.7	11
Fe	3.1	3.3	3.2
Ni		29	61
Cu		70	160
Zn		300	560
Br		750	2700
Pb		1100	2800

Titanium was selected as the reference element in this data set since it is likely that anthropogenic sources (mainly smelters) contribute relatively more to Fe than to Ti. From the scatter diagrams in figure 3 it can be seen that the Ti and Fe concentrations in the coarse mode are very closely related. The slope of the line in the figure represents the ratio between Ti and Fe according to Bowen (1966). Assuming no fractionating effects and the enrichment factor for Fe being around 3 indicate that Fe might have larger additional sources than Ti. If the reference element has non soil-derived components of the same order of magnitude or larger as the soil-derived component it is not meaningful to calculate enrichment factors. This is more likely to occur in the fine mode than in the coarse mode. From this data set it can not be concluded whether or not such sources exist.

Fig 3. Scatter diagram of Ti versus Fe in the coarse (1-8 μm) particle mode.



Enrichment factors in the fine mode ($<1 \mu\text{m}$) are only given for potentially soil-derived elements. These enrichment factors point to at least K and Mn having additional sources for particles in this interval. The remaining elements in table 3 all have high enrichment factors (80-8000) in the submicron range which indicate dominating anthropogenic or other natural sources. In the particle interval $1-8 \mu\text{m}$, Fe and possibly also K, Ca, V and Mn, have the same source as Ti (soil dust). The enrichment factor is much higher for the rest of the elements listed, indicating that other sources must also contribute in this interval. Whether these high enrichment factors are caused by condensation or coagulation reactions in the atmosphere or on the ground, or whether, fractionating effects exist can not be concluded. The high enrichment factor for Cl is probably caused by sea spray. Enrichment factors for the whole size range (up to $8 \mu\text{m}$) are also given in table 3 for comparison with earlier enrichment factors obtained from total filter measurements.

Comparisons of the enrichment factors in the two size intervals can give additional information to resolve whether a specific element has additional sources or if the eolian soil dust composition used is non representative. As mentioned earlier, K and Mn probably have additional sources contributing to the fine mode while not so strong indications of additional sources are found in the coarse mode. Fe has almost equal enrichment factors in both modes indicating the non representativeness of the soil composition used but can also be the result of fractionation effects.

Sector analysis

The samples were grouped according to the history of the corresponding air parcel. For a proper classification the following information was considered:

- i) 48-hour back trajectories for every six hours at the 850 mbar level (obtained through the Norwegian Institute for Air Research).
- ii) daily synoptic surface weather maps covering northern Europe (issued by the Swedish Institute of Meteorology and Hydrology).
- iii) recordings of the local weather situation at the sampling site.

Samples obtained during reasonably stable (in time) conditions were assigned into one of the five sectors shown in fig. 4. About 30% of the cases could not be classified in this way because of undefined trajectories or that the trajectories passed over several sectors.

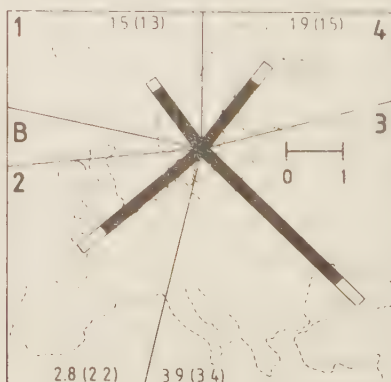
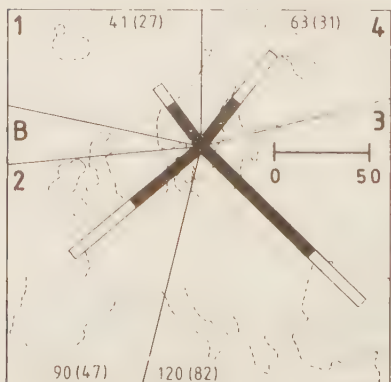
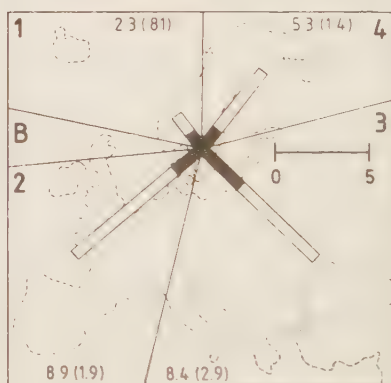
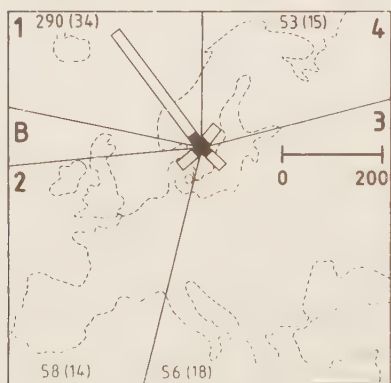
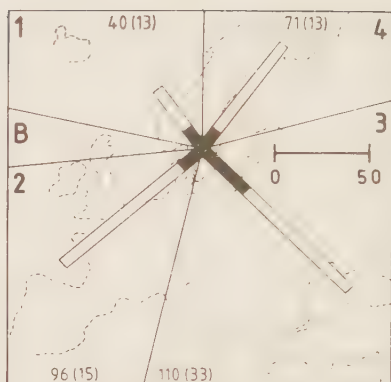
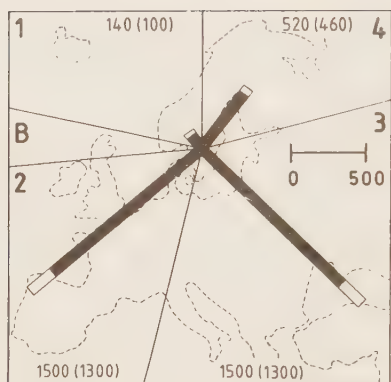
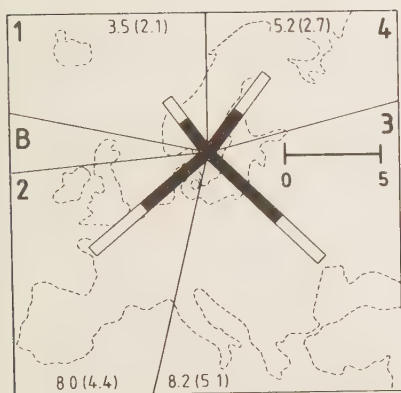
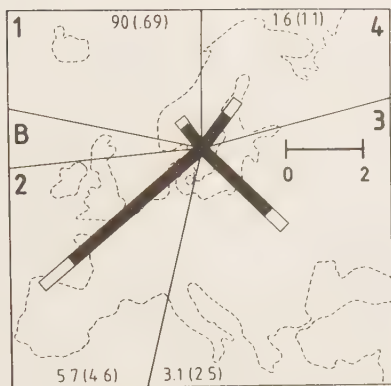


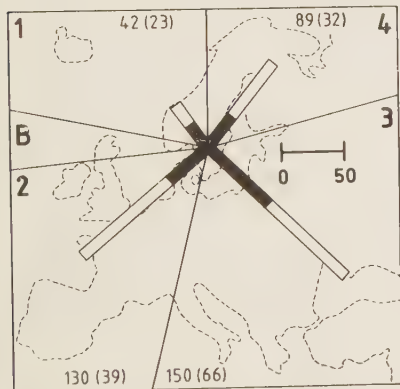
Fig 4a. Average concentrations in four sectors. The filled part of the bar refers to the fine ($<1 \mu\text{m}$) mode and the open part to the coarse ($1-8 \mu\text{m}$) mode. The numbers given are average total and within brackets fine mode concentrations (ng/m^3) in each sector. Please note that different components have different scales.



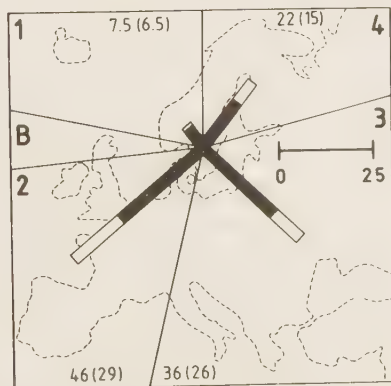
Mn



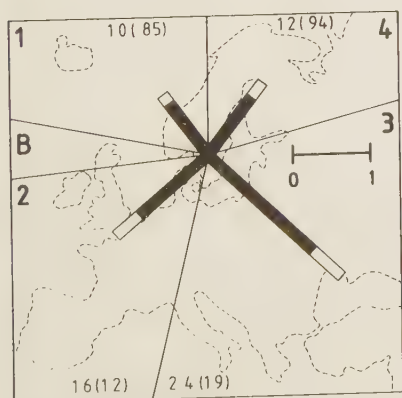
Cu



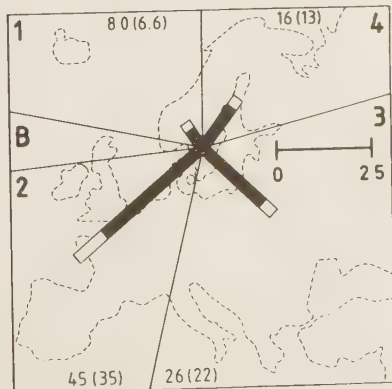
Fe



Zn



Ni



Pb

Fig 4b. Average concentrations in four sectors. The filled part of the bar refers to the fine ($<1 \mu\text{m}$) mode and the open part to the coarse ($1-8 \mu\text{m}$) mode. The numbers given are average total and within brackets fine mode concentrations (ng/m^3) in each sector. Please note that different components have different scales.

The borders of sector 1 are carefully selected so that this sector only contains "clean" air samples (i.e. low sulphur values). It was not possible to obtain a well defined border between sectors 1 and 2 and we have consequently located a "buffer" sector (B) between 1 and 2 which contains both rather "clean" and "polluted" samples while most of the samples in sector 2 show high concentrations of air pollutants. The divisions between sectors 2 and 3 and between sectors 3 and 4 are less critical. Sectors 2 and 3 are intended to show air pollutants from west and east of Europe respectively. Sector 4 is most likely dominated by sources in Sweden with some contribution from Finland and the Leningrad area. This will be discussed in a following paragraph. The width of sector B (~20 degrees) can be regarded as an estimate of the precision in trajectory calculations. It must be remembered that there is a limited number of samples in each group (about 15) and that some bias can occur with regard to source strength and dilution capability (since time of the year, windspeed and other factors are not evenly distributed between sectors as shown below).

The mean concentration of each element in each sector is shown in figure 4 and does - to some extent - reflect the relative source strength in the sector weighted by distance. The elements Cr and Br are not included since their values are very close to or below the detection limits in sectors 1 and 4 and are therefore very uncertain.

We can distinguish at least three different patterns in figure 4 with regard to the dependence of trajectory direction. Sulphur shows the strongest directional dependence - really low concentrations in sector 1, high in both sectors 2 and 3 and rather low in sector 4. For Cu, Zn and Pb the concentrations in sector 1 and 4 are also much lower than in sector 2 which is also somewhat higher than in sector 3. K, Ca, Ti, V, Mn, Fe and Ni have a weaker directional dependence, about equal concentrations (especially in the accumulation mode) for most of these elements in sectors 1 and 4 and lower than in sector 2 which is here somewhat lower than in sector 3. Concentration of Cl in the accumulation mode is essentially independent of trajectory orientation.

For Ca, Ti and Fe in the coarse particle mode we notice that the concentration is about equally high in sectors 2 and 3, a factor 2 lower in sector 4 and still lower in sector 1. It is also interesting to note that the directional dependence is not the same for the submicron fraction of these components - here concentration in sector 3 is almost twice that in sector 2. In the coarse particle mode, however, which is the dominant fraction of these components in the accumulation mode, the concentrations are about equal in sectors 1 and 4 and lower than in sector 2.

sector) which is to be expected with the Atlantic as a strong source.

Comparing sectors 2 and 3 (west and east of Europe) we find no major differences. The sulphur concentration is for instance almost the same. If anything, Cu and Pb seem to be somewhat higher in sector 2 while V and Ni are somewhat higher in sector 3. With regard to possible bias and the influence of Swedish sources discussed in the following paragraph we can not infer any differences in emission profile between the west and east of Europe from the present study.

The relative contribution from each sector to the grand average concentration for some elements is given in figure 5 which thus shows the relative importance of sources in a particular sector when the frequency of occurrence (see table 4) is also considered. The "undetermined" sector consists of samples taken during calm conditions or when a set of trajectories could not be assigned to a particular sector. This sector contributes most to the grand average. Air parcels with trajectories in sectors 2 plus 3 contribute 40 - 50% of the grand average for the elements S, Ti, Fe, Cu, Zn and Pb although the frequency of occurrence is only 23%. The high chlorine contribution from the buffer sector should be noted.

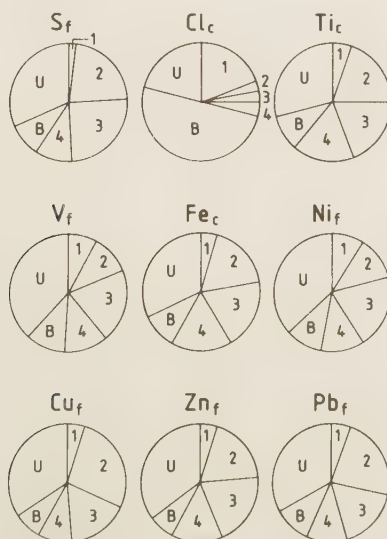


Fig 5. Relative contribution from each sector for some of the components (in the fine (<1µm) or coarse (1-8µm) mode) to the one year average concentration.

Table 4. Frequency of air masses in the different sectors.

Sector	1	2	3	4	B*	U**
Frequency	12	11	12	16	17	32 %
Angular fraction of sector	21	20	32	21	6	- %

*Buffer sector, **Unclassified samples

Contribution from Swedish compared to foreign sources

In a paper by Shaw (1981) a simple atmospheric dispersion model was applied to the data-set described in this paper. The model assumes that the emission from a source is spread and advected within a certain sector, well mixed within the atmospheric boundary layer. At a certain point the concentration is given by

$$c = \frac{Q(1-L)}{u \cdot H(\theta \cdot r + y)}$$

where Q = emission rate

L = loss term due to deposition, chemical transformation etc.

u = horizontal wind velocity

H = height of atmospheric boundary layer

θ = dispersion angle

r = distance from source to measuring point

y = width of source perpendicular to wind direction

The following assumptions were used for the calculations:

$\theta = 0.5$ radians,

L = 0 (except for lead where it was set to 0.2),

sector 4 concentrations were entirely the result of emissions within

Sweden except for S and Pb where Finnish sources were also considered.

The calculated concentrations for 11 of the samples (those with no precipitation) classified in sector 4 agreed with the measured concentrations within a factor of 3 for particles with a diameter less than $2 \mu\text{m}$ (see table 5a). The modelling technique was then applied without change to 13 of the samples classified into sectors 2 and 3 (see table 5a). Using these data and assuming no foreign (except from Finland) contributions in sector 4, a

comparison was made between the average of the ratios of measured to calculated concentrations in sector 4 with those in sectors 2+3 (see table 5b). The comparison suggests a substantial influence from foreign sources which is well above the uncertainties in the calculations. Swedish sources included in the calculations can thus only account for 10 - 30% of the concentrations measured in the southerly air-masses (i.e. sectors 2 and 3).

Table 5a. Average ratio measured/calculated concentrations in sectors 4 and 2+3.

	S	V	Ni	Pb
Sector 4*	1.8	0.94	1.5	3.0
Sector 2+3*	19	3.9	6.4	10

* Based on 11 (sector 4) and 13 (sectors 2+3) selected samples taken during stable (in time) atmospheric conditions and when no precipitation had occurred in the air masses sampled.

Table 5b. Approximate Swedish contribution in sectors 2 + 3 for particles <2 μ m (calculated from table 5a).

Average Swedish contribution (%)	S	V	Ni	Pb
in sectors 2 & 3	9.5	24	23	30

In view of these results it may be of interest to calculate the contribution from Swedish sources to the yearly average concentration element by element. Based on the box model approach (basically the same concept as used by Shaw) the long-term average concentration C is obtained as:

$$C = \frac{Q(1-L)}{u \cdot H \cdot r \cdot 2 \pi}$$

where the following parameters have a different meaning than earlier defined

Q = yearly emission

u = average wind speed at 100 meters

r = source strength weighted average distance

The following assumptions (calculations) were used in the box model approach:

L = 0

u = 5 meters/second

H = 1200 meters

r = 260 kilometers

These numbers are chosen to overestimate rather than underestimate the contribution from Swedish sources. In the calculation of sulphur emissions 3% original conversion to sulphate and then 1% per hour have been used. Thus about 16% of the emitted sulphur is in the form of sulphate at the measuring site. The choice of $L = 0$ is a rough approximation, partly supported by discussion in a later paragraph. The results of the calculations are shown in table 6.

Table 6. Comparison of the calculated and measured submicron concentrations at the Sjöängen sampling site giving the relative Swedish contribution.

Element	Yearly* emission ton/year	Calculated concentration ng/m ³	Measured concentration ng/m ³	Contribution Swedish sources %
S	250000**	130	680	20
V	460	1.5	2.1	70
Ni	180	0.59	1.2	50
Pb	1600	5.2	17	30

*references: S: K.H.M. (1981)

V, Ni and Pb: Liedholm et al (1981)

** of which 16% is transformed to sulphate at the sampling site.

The foreign contribution of sulphur to the wet and dry deposition in Sweden was estimated to be 70% in the OECD-report. In this report the calculations yield a value on the same level. In addition we also show that foreign sources play an important role for the concentrations in southern Sweden of some of the trace metals discussed in this work. This is in particular the case for Pb but to somewhat less extent also for Ni and V and is a result of the large emissions in central Europe and U.K., and a long enough residence time for the particulate material to be brought in over Sweden. Vanadium appears to have a somewhat lower relative foreign contribution than nickel. We cannot explain this difference though both V and Ni have their main sources in fossil fuel combustion, although fuel of different type and origin might be used. However, this difference is probably insignificant and can be regarded as an indication of the uncertainties in the calculations.

Seasonal variation in elemental concentration

A seasonal variation in elemental concentration can be expected as a result of changes in emission rates, transportation processes and dispersion efficiency during the year. The amplitude and phase of such variations can be expected to be rather specific for some groups of elements. In order to study the seasonal elemental concentration variation, mean concentration values were calculated for four periods: winter, spring, summer and fall. The sector classification of samples taken during the different seasons is given in table 7. The fall season contained most cases with air masses originating in sector 2 or 3, in the year of sampling. Air masses arriving from the north Atlantic (sector 1) occurred least during the spring and summer while air masses in sector 4 occurred most frequently during the summer. Calm conditions and meteorological changes caused 37% of the summer and winter samples to be "unclassified". As a measure of the "episodicity" the frequency of high values during each season was calculated (number of cases during a "season" with concentrations in the upper quartile of all cases), see table 8. The highest frequency of such values for most of the anthropogenic components were found in the winter while only few were observed during the summer. It is interesting to note that although the frequency of air masses from sectors 2 and 3 are highest in the fall this is not reflected in a high episodicity as shown in table 8 for this season.

Table 7. Seasonal frequency of samples in the different sectors.

Sector	Winter	Spring	Summer	Fall	Total no
1	6	2	1	5	14
2	2	1	3	6	12
3	3	4	1	6	14
4	2	6	9	1	18
Buffer	2	5	8	4	19
Unclassified	14	9	8	5	36
Total no	29	27	30	27	113

Seasonal mean concentrations are shown in figure 6 and reveal a quite consistent picture. The lowest concentrations for almost all elements in both the fine and coarse modes were found during the summer. Most of the components of anthropogenic origin (high enrichment factors) show a substantial seasonal

Table 8. The seasonal "episodicity" of the total elemental concentrations defined as the number of cases in the upper concentration quartile of all samples for each element in each season.

	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Winter	8	10	8	6	9	16	12	14	10	15	15	14	15	15
Spring	13	7	11	13	11	10	11	10	12	11	9	9	7	7
Summer	3	6	3	4	2	0	2	1	2	0	0	1	1	1
Fall	4	5	6	5	6	2	3	3	4	2	4	4	5	5

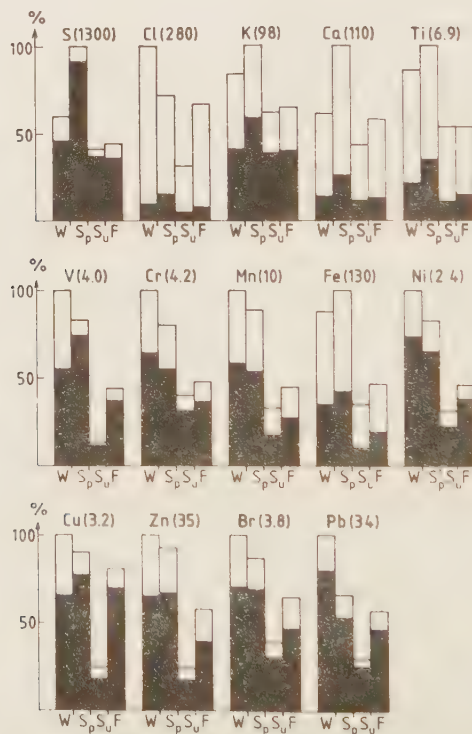


Fig. 6. Seasonal average elemental concentrations normalised to the highest concentration (given in brackets in ng/m³) for each element. The filled part of the bars refers to the fine (<1 μm) mode and the open part to the coarse (1-8 μm) mode.

dependence with highest values in the winter, while most of the soil-derived components have a less pronounced seasonal variation with the highest values during the spring. The high ratio of winter to summer concentrations can be explained as principally due to meteorological factors, in particular a greater vertical dispersion in the summer, perhaps combined with somewhat

higher emission rates during winter (at least for components associated with fossil fuel combustion) and a more efficient (includ) removal rate during the summer. In the case of sulphur this effect (further enhanced by lower dry deposition of sulphur dioxide during the winter) is compensated by a much more rapid oxidation rate of SO_2 to sulphate during the summer. Also the soil-derived component may fit into this picture assuming a higher suspension rate during non-winter conditions but also a much more efficient (dry) removal rate. In the case of chlorine, a weaker source strength during the summer should also be considered.

Dry deposition

The available data-base is well suited for an estimate of the dry deposition if combined with a so called dry deposition velocity (v_g). Ideally we need to assign values to v_g with regard to particle size distribution, ground cover and meteorological conditions. Such values are not known with great accuracy even for a uniform area and well defined meteorological conditions and will, of course, be even more uncertain for long term averages for the real landscape. Extensive overviews (e.g. Sehmel 1980) have demonstrated the uncertainty. For short vegetation and particle diameters of $0.1 - 1 \mu\text{m}$ predictions usually give values of less than 0.05 cm/s for v_g (i.e. Garland 1977, Davidson and Friedlander 1978 and Sehmel 1980). For $2 \mu\text{m}$ particles, for example, these authors give estimates of 0.06 , 0.02 and 3 cm/s respectively. For tall vegetation and accumulation mode particles Hicks (1980) summarises: $v_g = 0.1 \text{ cm/s}$ represents the conventional viewpoint, $v_g = 0.4 \text{ cm/s}$ represents the most likely long term average for northwestern continental USA, $v_g = 1.0 \text{ cm/s}$ is the highest value likely to be appropriate as a long term average over any normal surface in the continental USA. For an estimate of the deposition velocity of particles larger than $1 \mu\text{m}$ diameter for tall vegetation we have essentially relied on work by Chamberlain (1975).

From a balance of evidence - from the literature and our own experience - we have adopted the numbers for v_g given in table 9 as valid for a coniferous forest. They will be somewhat smaller for short vegetation. With the size distributions given in figure 2 we can now calculate a particle size weighted mean deposition velocity and then the yearly dry deposition (table 10). Wet deposition to the same area is estimated from measurements at Sjöängen (Cranat, unpublished data). Also considered are trace metal analysis in Denmark (Hovmand 1979) and Norway (Semb 1979).

Table 9. Dry deposition velocity used for estimating the dry deposition to a forest.

Particle diameter	Deposition velocity
μm	cm/s
0.06 - 0.25	0.3
0.25 - 0.5	0.2
0.5 - 1.0	0.3
1.0 - 2.0	0.5
2.0 - 4.0	1.
4.0 - 8.0	4.

Table 10. Estimated dry deposition to a forest compared to measured wet deposition.

	Particle size weighted dry deposition velocity*	Dry deposition	Wet deposition
	cm/s	$\text{mg}/\text{m}^2\text{year}$	
S	0.40	100	900
Cl	1.8	100	500
K	0.86	21	100
Ca	1.6	38	200
Ti	1.4	2.3	5
V	0.45	0.35	3
Mn	0.72	1.5	6
Fe	1.1	31	20**
Ni	0.56	0.27	2
Cu	0.53	0.39	4
Zn	0.48	3.6	20
Pb	0.41	2.7	15

* for particles < 8 μm diameter.

** very uncertain

Despite the uncertainty in the calculations we can conclude that for most of the elements the dry deposition is of minor importance than the wet deposition, especially for those elements which have most of the mass in the accumulation mode (S, V, Ni, Cu, Zn and Pb) and also for Cl, K and Ca. For some of the large particle oriented elements i.e. Ti and Fe the dry deposition is on the same level as the wet deposition. In reality the dry deposition may be larger since particles larger than 8 μm were not considered in this estimate.

CONCLUSIONS

It was found that the fourteen elements which were studied in this investigation could be conveniently divided into four groups each with the following characteristics:

1) S, V, Ni, Cu, Zn, Pb and to some extent Mn have high enrichment factors relative to Ti and a strong seasonal variation with the highest concentrations during winter (except for S, where chemical reactions in the atmosphere counteract this variation). Most of the mass is found in the accumulation mode although there is some difference in the size distribution where V and Cu have the lowest median diameter and Mn and Zn the highest. The components are mainly of anthropogenic origin. We may not rule out that some of the submicron Ca, Ti and Fe may belong to this group although the indications are rather weak.

The highest concentrations and the largest relative contributions to the yearly averages for Cu, Zn and Pb occur in sector 2 (when the unclassified samples are not considered) which includes sources in western Europe. A similar comparison in sector 3 including sources in eastern Europe yields V and Ni. The sulphur concentration is about equally high in these two sectors.

The wet deposition is approximately one order of magnitude higher than the calculated dry deposition.

Swedish sources may contribute of the order of one fourth to one half to the yearly average concentration as found at Sjöängen for the elements S, Ni, and Pb but some two thirds in the case of V.

2) Ca, Ti and Fe have low enrichment factors, most of the mass in the coarse particle mode (1-8 μm) and a weaker seasonal variation of the concentration with the highest values in the spring and the lowest values in the summer. The concentrations found in sectors 2 and 3 are on the same level which is a factor of 2-4 higher than in sectors 1 and 4. Dry deposition for Ti and Fe is on the same level as the wet deposition, while the wet deposition is dominant for Ca. Most of the mass of these elements is soil-derived.

3) Cl has a high enrichment factor, a strong seasonal variation with the

lowest concentrations in the summer, the highest concentrations in the buffer sector, most of the mass in the coarse particle mode and dominating wet deposition. The main part of this element originates probably from seaspray with the Atlantic as the major source and with some contribution from the Baltic.

4) K has a quite high enrichment factor in the fine particle mode, an unusually broad size distribution, a small seasonal concentration variation and dominating wet deposition. We are presently not prepared to suggest the most important source or combination of sources for this component, but soil and seaspray are two of the possible contributors.

Cr and Br are based on rather incomplete data but would tentatively be placed in groups 1 and 3 respectively.

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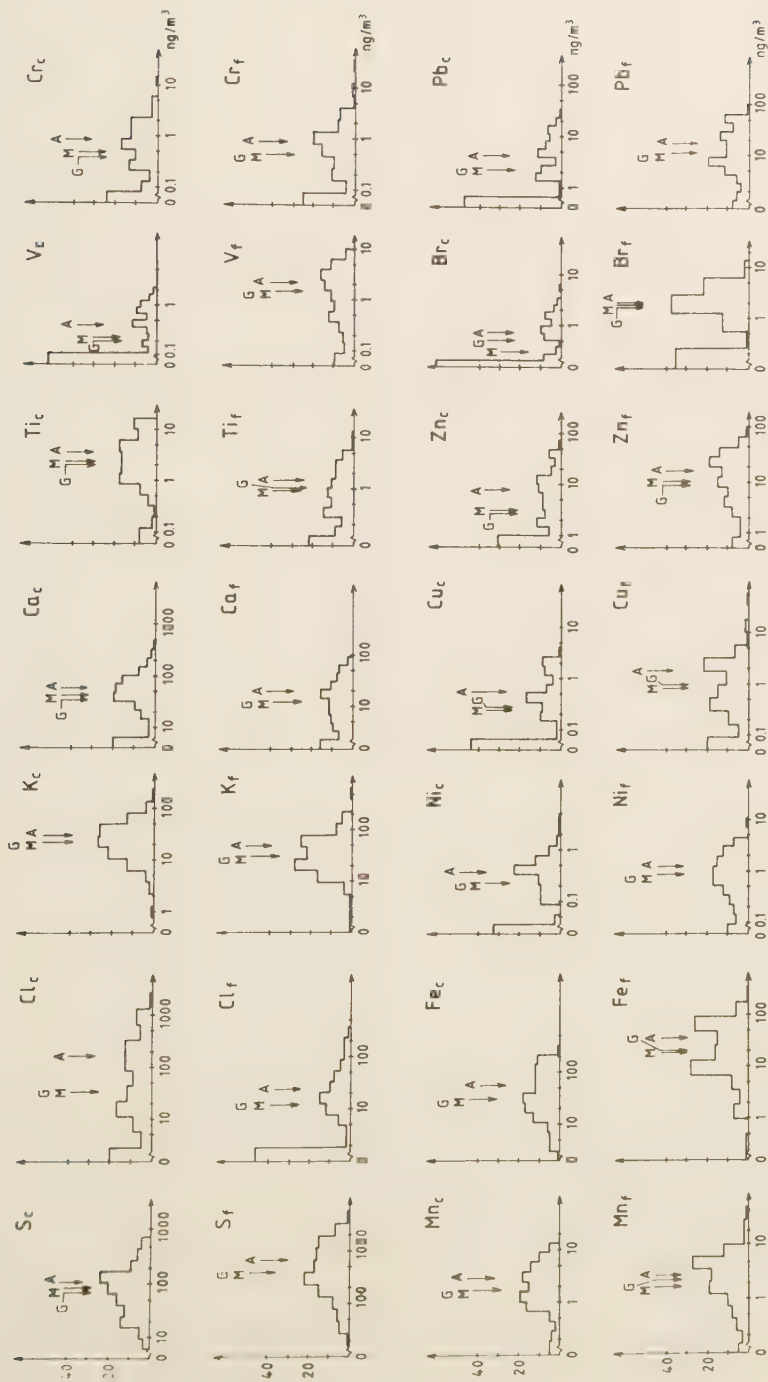
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APPENDIX

The frequency distribution of elemental concentrations for the fine and coarse particle size intervals (<1 and 1-8 μm aerodynamic diameter) are shown in the figure. The graphical display shows the average elemental concentration per logarithmic concentration interval. The numbers displayed in the graph are actual concentrations and the number of cases in each concentration interval. Also indicated are the geometric mean, the arithmetic mean and the median.

In a log-normal distribution the median (M) and the geometric mean (G) should coincide and the arithmetic mean (A) can be derived from $A = M * \exp(\sigma_g^2/2)$ where σ_g is the geometric standard deviation. In the figure it can be seen that M and G often are very close. The arithmetic mean is often a factor of 2 higher than M which according to the equation above gives a $\sigma_g = 1.2$. However the calculated σ_g 's are between 2 and 3. This indicates a skew log-normal distribution for some of the elements. In some cases this can be explained as 'disturbances' from the detection limit.



Paper IIIINTERELEMENT AND MULTI-STATION CONCENTRATION EVIDENCE FOR LARGE SCALE AEROSOL
SULFUR TRANSPORT ACROSS SWEDEN

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Interelement and multi-station concentration evidence for large scale aerosol sulfur transport across Sweden

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ABSTRACT

The concentrations of sulfur and several more elements were measured in a network of six sites in southern Sweden. High time resolution samples were taken using a continuous filter sampler and analysed by particle induced X ray emission (PIXE). Simultaneous increases in the sulfur concentrations were seen along the network due to the inflow of polluted air masses. High sulfur concentrations generally occurred during south-westerly to easterly air flow. Some of the episodes, distinguished by their shorter duration and their elevated vanadium and nickel concentrations, are suggested to be of local origin.

1. Introduction

Interest in the possible long range transport of air pollution over distances greater than 1000 km has focused on sulfur in the form of gaseous SO₂, sulfuric acid and sulfates (Sweden's case study 1971, Rodhe et al., 1972; Brosset 1973). In the OECD study on long range transport of air pollutants (OECD, 1977), an estimate of a European budget for the total deposition of sulfur in 1974 has been made. The results show that large amounts of sulfur pollutants are transported over long distances under certain meteorological conditions. Furthermore, countries like Finland, Norway and Sweden receive considerably larger amounts of air pollution from abroad than are emitted within these countries (Ottar, 1977).

A comparison of chemical and meteorological data ideally should be made using aerosol sulfur concentration measurements with a time resolution comparable to the time variations in air flow pathways. The frequently employed strategy of sampling suspended particulate matter for 24-h periods often averages concentrations over different meteorological conditions of possible importance to pollution transport. Consequently, a time

resolution of less than 24 h for aerosol sampling may be a desirable improvement. The present investigation was undertaken as a field test of such a strategy.

It is important to distinguish between contributions from nearby pollution sources and the larger scale transport of pollutants from more distant sources. A short time resolution, such as employed in this study, may permit the identification of periods when concentrations are influenced by plumes from local air pollution emissions. A complete investigation of air pollution sulfur transport, of course, should include measurements of both gaseous and particulate forms of sulfur. In this investigation, however, only the aerosol was sampled for elemental analysis.

2. Experimental

Six sampling sites in southern Sweden were chosen for this investigation. These sites, with locations shown on the map (Fig. 1), are among those chosen for the precipitation sampling network operated by the International Meteorological

LARGE SCALE AEROSOL SULFUR TRANSPORT ACROSS SWEDEN



Fig. 1. Map showing six aerosol sampling locations in Sweden at Stockholm, Ryda Kungsgård, Grimsö, Velen, Rörvik and Ekeröd.

Institute in Stockholm (IMI-network) and are fully described elsewhere (Granat et al., 1977).

The sampling was generally carried out several meters above ground, at locations with negligible obstructions in the neighborhood. The samplers used were of a special continuous time sequence design (Nelson et al., 1976). These "streaker" samplers consist of an orifice which moves with a constant speed along a Nuclepore filter strip. Air is drawn through the orifice at a rate of 0.8 l/min. Hereby a 5-mm-wide streak of aerosol deposit is left on the filter. Consecutive 2-mm spots of the streak are analysed, resulting in a time resolution of approximately 2.4 h of sampling time. The uncertainty in the absolute time determinations of single spots are less than ± 1 spot = 2.4 h.

Particle induced X-ray emission, PIXE (Johansson et al., 1975; Johansson & Johansson, 1976), has been used for the multi-elemental

analysis of the streaker filter samples for sulfur and other elements ranging in atomic number from silicon to lead. In this investigation the elements Si, Cl, K, Ca and Fe in addition to sulfur, were usually seen above their detection limits in the samples. The analysis was performed by placing a filter strip, representing 8 days of sampling time on a single strip, into a vacuum chamber of the Van de Graaff accelerator at Florida State University and analysing successive steps by detecting X-rays generated during bombardment by 5 MeV protons. The X-ray spectrum from each analysis was recorded electronically during the approximately 1 min of proton bombardment time per step and later resolved into elemental constituents by computer procedures (Kaufmann et al., 1977).

The quality of the PIXE analysis is ensured by analysing standards during each accelerator run. Aerosol samples have been analysed repeatedly

revealing no changes in the composition of the elements reported here. However, recent data (Hansen et al., 1980) points out that in pre-concentrated samples losses of volatile sulfur species and losses induced by the proton irradiation can occur. These effects seem to be most serious for some sulfites. Atmospheric aerosol samples collected at a remote location on Nuclepore filters and analysed by PIXE have been compared with samples collected simultaneously on Acropore filters and analysed by the Thorin method at the Department of Meteorology, University of Stockholm. The results show an agreement between elemental sulfur from the PIXE-analysis and sulfate analysed wet chemically within $\pm 10\%$ in 75% of the samples (within $\pm 5\%$ in 50% of the samples). Since the X-rays emitted from sulfur atoms are relatively soft, self-absorption problems have to be considered. In this study the maximum aerosol deposit on the filter was 0.1 mg/cm^2 causing a negligible self-absorption of sulfur X-rays (Johansson et al., 1975). Large aerosol particles can also cause self-absorption losses, e.g. for a $5\text{-}\mu\text{m}$ diameter particle the self-absorption would be approximately 5%. The pollution-derived sulfur-containing particles are found in the accumulation mode with a mass median diameter of $0.2\text{--}0.4 \text{ }\mu\text{m}$ (Whitby, 1978). This implies that except for sea spray-derived sulfur-containing particles (larger than $2 \text{ }\mu\text{m}$) no absorption effects can be expected. The detection limit for sulfur was set primarily by the thickness and composition of the filter material and averaged about 150 ng/m^3 . Since concentrations observed in this study ranged from several hundred to several thousand ng/m^3 , sulfur was detected in all samples. However, certain other elements of interest, including vanadium and nickel, were only occasionally found above their detection limits.

The high sensitivity of the PIXE method in combination with the small sample requirements makes this method useful for the analyses of many types of samples. Since only a small sample ($\sim 10 \text{ }\mu\text{g}$) needs to be collected, light weight and portable sampling devices may be employed, requiring small vacuum pumps with modest electrical power requirements. Depending on the information needed, different combinations of time, particle size and site-to-site distance resolution can be used. In a standard type 12–24 h aerosol sample (total filter or cascade impactor), 10–20 elements heavier than

phosphorus can be resolved in a 1–3 min routine analysis. On the sacrifice of a few elements and size distribution information, a time resolution of a few hours can be achieved. A streaker sampler can operate in rural or remote air with time resolutions from 2 to several hours. Since each streaker filter will contain samples collected over a week or more, its infrequent changing makes this sampler very easy and inexpensive to operate. The streaker sampler with a suitable time resolution, used in conjunction with PIXE analysis, is therefore ideal in many respects for use in air pollution sampling networks.

3. Results

Two sampling periods, each of 8 days' duration, in the spring of 1978, were selected for this study. The meteorological conditions included airflow from both northerly and southerly directions and therefore provided an opportunity to compare the composition of air passing over strong pollution source regions with that from less polluted areas. Fig. 2 shows 96 h back trajectories for air masses at the 850 mbar level, calculated by the Norwegian Meteorological Institute. Surface weather maps from the Swedish Meteorological and Hydrological Institute are shown in Fig. 3. The significance of the weather data is discussed further below in connection with the sulfur concentration data. In Fig. 4 the measured concentrations of aerosol sulfur are shown on a linear scale as a function of time of sampling. In all cases the concentrations varied markedly with time over a total range of up to a factor of 10, with large variations taking place frequently over a few hours. As the following discussion will make clear, some of the high sulfur concentration episodes may be due to local air pollution passing over the sampling sites, whereas other episodes appear to be large scale effects apparently due to sulfur transported over long distances.

One indication of the presence of a local sulfur plume (resulting mainly from the combustion of fuel oil) can be found by examining relationships between sulfur and other trace elements emitted from the same type of sources. Fuel oil often contains vanadium and nickel. The concentrations vary somewhat depending on the origin of the oil. The sulfur emissions are initially mainly in the form

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Fig. 2. A-F. Selected (representative) 96 h air mass trajectories at the 850 mbar level. The numbers indicate year, month, day and hour.

of sulfur dioxide gas which is gradually converted to sulfates at a rate depending, e.g. on the pollution level, and typically in the range of 0.1 to 10% per hour (Boulard et al., 1978; Calvert et al., 1978; Harrison et al., 1975). Vanadium and nickel are

already at the point of emission in particulate form. Unpublished data from a study undertaken by Lannefors and Hansson in the middle of Sweden, show that sulfur, vanadium and nickel have almost identical particle size distributions with almost all

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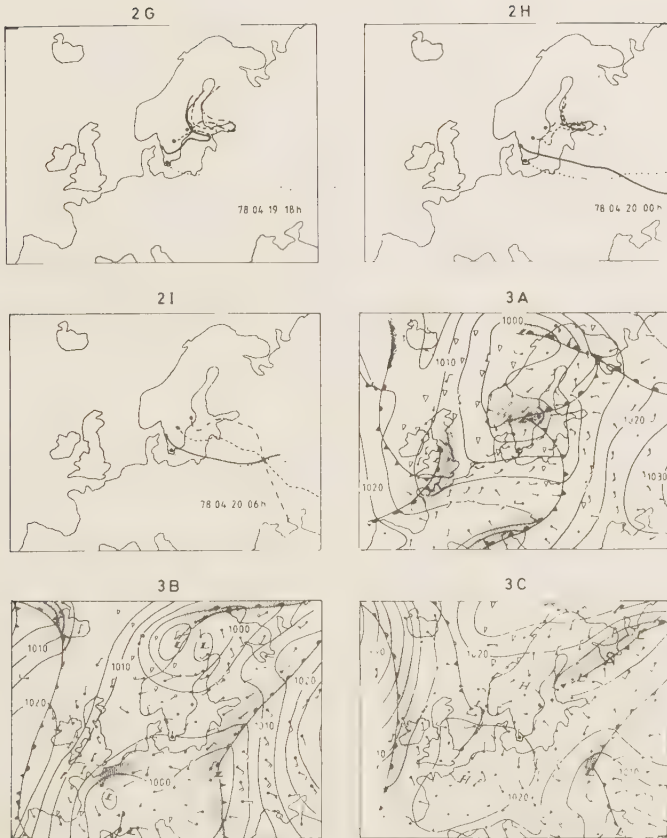


Fig. 3. A–C. Surface weather maps at 0600Z on April 12, 14 and 19, 1978.

the concentration in the accumulation mode. These results are in agreement with those of Charlson et al. (1978) stating coexistence of vanadium, nickel and sulfates on particles in the accumulation mode. Evidently these elements exist on particles having

the same size distribution and maybe also on the same particles. This implies that the sulfate deposition velocity should not differ very much from that of vanadium and nickel. However, since sulfur dioxide is gradually converted to sulfate

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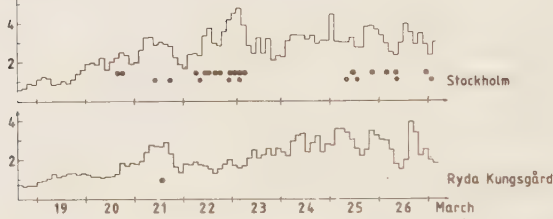
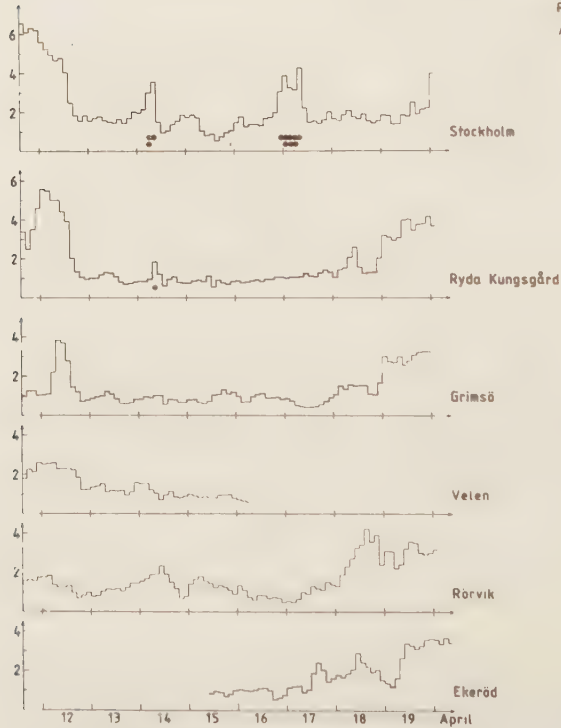
Sulfur concentration
 $\mu\text{g}/\text{m}^3$ PERIOD 1
March 18-26, 1978PERIOD 2
April 11-19, 1978

Fig. 4. Time variations of aerosol sulfur concentrations measured every 2.4 h at two sampling sites, March 18-26 and at six sampling sites, April 11-19, 1978. Periods of high V ($>100 \text{ ng}/\text{m}^3$) and Ni concentrations ($>60 \text{ ng}/\text{m}^3$) are indicated by dots (●) for V and circles (○) for Ni.

during the atmospheric transport, the ratio of sulfur to vanadium (or nickel) should increase with the transport distance.

Another indication of influences from local sources is the existence of nonsimilar concentration patterns at different sampling locations.

The Stockholm site and also the nearby Ryda Kungsgård site exhibited short-term sulfur concentration maxima during which significantly increased concentrations of nickel and vanadium were observed. At Stockholm, three pronounced episodes, March 22–23, April 13–14, and April 16–17 1978, were seen during which a correlation of sulfur with vanadium and nickel was found. One of these episodes is illustrated in Fig. 5. Sulfur concentrations reached their highest values during the night and early morning of the April 16–17 episode, when vanadium and nickel also were found substantially above their detection limits. From these results, and by examination of the time

variations at the Stockholm site, it appears that a substantial part of the total observed sulfur concentration during these episodes may be attributed to local plume sources.

Precipitation occurred during several of the sampling days and mostly during March. However, during the 12-h periods when precipitation was recorded, only minor amounts fell (i.e. less than 5 mm and usually also less than 1 mm in 12 h); probably causing only small effects on single elemental concentrations by aerosol particle scavenging. The conclusions made in this study are therefore probably not biased because of effects caused by precipitation.

Because of the frequent use of 24-h sampling routines, it is of interest to calculate from our results the 24-h average sulfur concentration seen on each of the sampling days. These are shown in Table 1 for the six sampling locations. The lowest average sulfur is less than 600 ng/m³ (equivalent to less than 1800 ng/m³ sulfate) and the highest is over 3000 ng/m³ (equivalent to over 9000 ng/m³ sulfate). Individual 2.4 h sulfur concentrations, however, reach as high as 6000 ng/m³ and as low as 400 ng/m³. Therefore, by smoothing over short time fluctuations, the 24-h averages exhibit less variability than is observed over shorter intervals, and episodes when local plumes contributed to the measured concentration may not be recognized.

4. Discussion

By comparing the air mass trajectories an attempt can be made to interpret the observed aerosol sulfur concentrations in terms of atmospheric transport from source regions. In Fig. 4 a striking resemblance is seen in many of the features of the time variability patterns at the different sampling stations in both the March and April periods. Except for the vanadium-related sulfur maxima seen in Stockholm (and also less distinctly at Ryda Kungsgård), the different sites show similarities. In the March 18–26 period at Stockholm and Ryda Kungsgård, concentrations are initially low and later relatively high. According to the air mass trajectories a generally north to northeasterly air flow persisted until noon March 20. A representative trajectory for this period is shown in Fig. 2A. On March 20 and 21 the air masses originated in the northern part of the European Continent and the western part of Russia

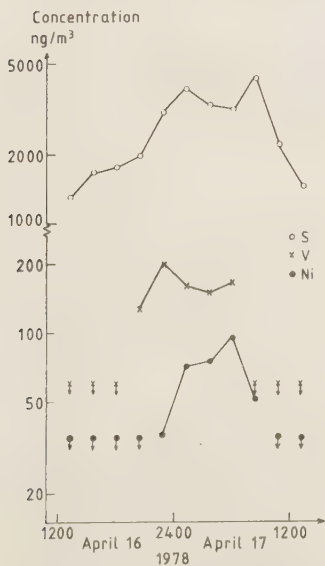


Fig. 5. Concentrations of sulfur, vanadium, and nickel observed at the Stockholm site on April 16–17, 1978. Detection limits are denoted by an arrow.

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Table 1. 24-h mean sulfur concentrations, ng/m³*

Date, March 1978								
Site	19	20	21	22	23	24	25	26
Stockholm	1050	2080	2720	2970	3180	3110	3350	3080
Ryda Kungsgård	1170	1360	2240	1700	2140	2790	3050	2610
Date, April 1978								
Site	12	13	14	15	16	17	18	19
Stockholm	3690	1630	1890	1120	1690	2470	1700	1890
Ryda Kungsgård	3490	986	988	808	896	1160	1613	3560
Grimsö	1870	849	811	912	874	588	1390	2970
Velen	2110	1260	1070	881				
Rörvik	1240	1150	1560	1370	796	1010	2910	3020
Ekeröd				869†	914	1490	2060	2730

* Arithmetic means of 10 observations per 24 h. Sulfate equivalent = $3 \times$ sulfur concentration.

† Based on only six observations

(see Fig. 2A). Higher sulfur concentrations (not related to vanadium and nickel) occurred during these days. Late March 21 the air flow again became north to northeasterly and the sulfur concentrations decreased. A local episode can be discerned in Stockholm on March 22–23. On March 23 the air flow changed to a south to southwesterly direction passing in over the British Isles and the northern part of the European continent (see Fig. 2A). The same flow persists throughout the first sampling period with only minor direction changes in the trajectories. Concentrations of sulfur were generally high but variable. The variations which can be seen at both locations can be accounted for by minor changes in the track of the air masses, sometimes passing in over the northern part of the European continent, sometimes passing over the North Sea (see Fig. 2A). Influences from local sources as well as precipitation scavenging can also help to explain these variations. The results above suggest that southerly flow is associated with higher sulfur concentrations (not related to vanadium and nickel) on a regional scale.

In the April 11–19 sampling period, observations were made at all six sites except for some electrical malfunctions during the first 3 days of sampling in Ekeröd and the last 3 days in Velen. As can be seen from a surface weather map (Fig. 3A) the weather situation on April 12 was dominated

by a circulation around a low pressure center in the middle of Sweden. This created a general inflow of air masses from the Norwegian Sea at the Rörvik sampling site. At the Stockholm, Ryda Kungsgård, Grimsö and Velen sites air masses that had passed over the European continent came in from south to the southwest (see Fig. 2B). As a result increased sulfur levels were seen at the latter sites (especially in Stockholm and Ryda Kungsgård), while the sulfur concentration at Rörvik remained low (see Fig. 4). Late April 12 the air flow changed somewhat not passing over the European continent or the British Isles (see Fig. 2C). This air flow remained until April 18 except for a period on April 15 and 16. During April 15 a flow around a low pressure center situated in northern Scandinavia developed, bringing up old continental air masses to the sampling network (see Fig. 2D). However, no effects can be seen on the sulfur concentrations. During the period April 13 to 18 (including April 15 and 16) the sulfur levels were low except for the two local episodes seen in Stockholm on April 13–14 and April 16–17. The weather maps for April 14 and 17, shown in Fig. 3B and 3C indicate very light winds and clear skies in the Stockholm area, thus reducing mixing and increasing the stability. These conditions are favourable for trapping local emissions, which can be seen as increased sulfur concentrations (related to V and Ni) during the night and morning of April 13–14

and April 16–17. When the first local (V-related) Stockholm episode is broken up, increased sulfur concentrations can be traced at the Ryda Kungsgård site.

On April 18 a complicated flow pattern started to develop. This included first a weak flow from northwest to west (see Fig. 2E) and then during April 19 an even weaker flow mainly from the north but taking different nonstraight paths to the sampling sites (see Fig. 2F). High sulfur concentrations were seen in Rörvik and Ekeröd and could also be traced at Grimsö and Ryda Kungsgård on April 18. Even higher sulfur concentrations (see Fig. 4) were found all over the network on April 19. The weak flow in combination with passages over source areas in Denmark and southern Sweden are possible explanations for those high sulfur concentrations. The accuracy of the calculated air mass trajectories could also be questioned during a complicated meteorological situation.

However, late April 19 and April 20 the situation straightened out and the flow was gradually altering to an easterly flow (see Fig. 2G, 2H and 2I), and the sulfur concentration level became high all over the network (see Fig. 4).

5. Conclusions

This comparison of sulfur concentrations obtained at simultaneously operated sampling sites suggests that large scale features seen in the time variation of the sulfur concentration are the result of long-range transport into Sweden of polluted air masses from a generally southwest to easterly

direction. Superimposed upon this are local emission effects (seen in Stockholm and Ryda Kungsgård), showing vanadium and nickel associations with sulfur, which may be attributed to sources in the Stockholm area. This study illustrates the advantage of combining a network of sampling sites with comparably high time resolution samplers (0.1 day). Good time resolution and multi-element analysis are needed in order to discern local episodes of short duration. Such a time resolution is also needed to study the flow patterns of the air masses at nearby stations. For long-range transport studies with the sampling sites located far apart, with no local sources, a time resolution of 12–24 h appears to be sufficient. Cascade impactors can thus be used, permitting a size classification of the aerosol (Johansson et al., 1976; Lannfors et al., 1977). In combination with multi-element analysis such as PIXE analysis, important information on possible pollution and natural sources can be obtained.

6. Acknowledgements

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КРУПНОМАСШТАБНЫЙ ПЕРЕНОС СЕРНЫХ АЭРОЗОЛЕЙ ЧЕРЕЗ ШВЕЦИЮ ПО ДАННЫМ ИЗМЕРЕНИЙ КОНЦЕНТРАЦИЙ РЯДА ЭЛЕМЕНТОВ НА СЕТИ СТАНЦИЙ

На сети из шести станций в Южной Швеции измерялись концентрации серы и нескольких других элементов. Пробы с высоким разрешением по времени брались с использованием непрерывного фильтрового заборника и анализировались с помощью рентгеновской эмиссии, возбуждаемой частицами. Последовательные увеличения в кон-

центрации серы наблюдались на сети станций при притоке загрязненных масс воздуха. Высокие концентрации серы обычно встречались при ветрах с юго-запада до востока. Локальные выбросы серы различались их более короткой длительностью и связью с повышенными концентрациями ванадия и никеля.

Paper IVTHE CHEMICAL COMPOSITION OF ARCTIC HAZE AT NY-ÅLESUND, SPITSBERGEN

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The chemical composition of arctic haze at Ny-Ålesund, Spitsbergen

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ABSTRACT

Samples of arctic haze particles were collected at Ny-Ålesund, Spitsbergen (12°E, 79°N) during late winter 1979. The filter samples were analysed wet chemically and by particle-induced X-ray emission (PIXE). The concentrations of 17 major ions and metals were determined and compared to previous results of arctic and antarctic research. Simultaneous measurements of the aerosol size distribution were used to check the consistency of the results. Both the chemical composition and the size distribution data support the hypothesis that the arctic winter aerosol is heavily influenced by a well-aged continental aerosol originating in midlatitude anthropogenic source areas.

1. Introduction

The continuously growing anthropogenic influence on the environment causes a need for establishing baseline or background values for the different trace substances in the atmosphere. The same need exists for optical properties of the atmosphere such as visibility or turbidity since the relationship between the physico-chemical properties of the atmospheric particulates and their optical properties has not yet been clarified completely.

Reliable baseline aerosol measurements are best accomplished as far away as possible from strong source regions. In the Northern Hemisphere this leads to the central regions of the North Pacific, the North Atlantic Ocean and the polar region. The maritime regions are not well suited for ground level aerosol measurements because the local sea spray component will influence the concentrations of many elements and compounds. Thus remains the arctic region. A closer look shows that extensive atmospheric studies are justified in the Arctic not only for global baseline monitoring but

also because of the specific regional character of the Arctic.

In winter, 90% of this vast area between North America and Eurasia is covered by ice and about 60% in summer. The pack ice floats like a thin film on the Arctic Ocean and causes the continental thermal character of the area. This pseudo continent has a surface albedo at about 80% but a reduction from 70 to 60% would destroy the pack ice in 8–10 years. A summer air temperature anomaly of +2 °C would cause the same destruction process in a few decades (Budyko, 1962). Global changes of climate are to be expected as a consequence of such a drastic change. Because of their scattering and absorption effects in both the solar and the terrestrial spectral regions, aerosol particles can contribute to an air temperature anomaly. In deposited form the particles can cause surface albedo changes. Imbedded in snow, absorbing particles can cause temperature changes in the snow layer.

During the winter period the arctic sink region provides a unique possibility for studying long-distance transport and transformation processes of continental aerosols emitted in Eurasian regions. On the 3000 to 5000 km long pathway from these

¹ Contribution No. 415.

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sources to the Arctic, the investigation of transport and transformation mechanisms are facilitated by the fact that the lower boundaries are snow- and ice-covered land and sea areas without significant gas or particle sources. The removal of atmospheric trace substances through precipitation is the most complicated aspect in long-distance transport studies. However, in the Arctic, precipitation in general is lower than in mid-latitudes and has its minimum in late winter or spring, again facilitating the study of aerosol transport. Despite these simplifying regional characteristics, only very few transport studies of the origin and the fate of the arctic aerosol have been done (Rahn et al., 1979c; Rahn, 1979b) and the results are still tentative.

A knowledge of the arctic air chemistry is needed for more quantitative modelling of trace substances in the Arctic. There have been a number of field studies mainly in Alaska (Rahn, 1971) and Greenland (Flyger et al., 1978).

Results from areas closer to the Eurasian source region (i.e. Spitsbergen, Franz-Josefs Land) have not yet been published and no serious attempt has earlier been made to combine measurements of physical (especially optical) and chemical properties of arctic haze particles. Recently a first analysis of chemical measurements in the Spitsbergen region has been presented by Larsson and Hansson (1979) on a WMO-Conference in Boulder, Co. In a field experiment conducted by one of the authors (J.H.) near Ny-Ålesund, Spitsbergen, in April-May 1979, *in-situ* measurements of the aerosol size distribution and integral optical properties were combined with the sampling of particles in two size classes for subsequent chemical analysis. Size distribution and optical properties have been reported in a previous paper (Heintzenberg, 1980). Here the results of the chemical analysis and an investigation of the air mass origin are presented. The internal consistency of the physical and chemical aerosol data is verified by comparing aerosol masses derived through the inversion of optical data with aerosol masses from chemical analysis.

2. Location and the problem of local contamination

The geographical coordinates of the sampling site Ny-Ålesund are 12° E, 79° N. Details about

the station are given by Heintzenberg (1980). The risk of local contamination is the most important problem connected with the sampling of atmospheric trace substances in extremely clean remote areas. During continuous atmospheric measurements, periods of local influence can usually be clearly identified and excluded from the data evaluation by distinct level changes or increasing variance of the recorded parameters. In contrast, the sampling of aerosol under background conditions can be much more seriously affected by local contamination. Even with high-volume samplers it may take more than 1 day of sampling to get enough mass for a chemical analysis accumulated on the filters. Short periods with elevated levels through local influence can spoil several days of sampling. There is no ideal background measuring station where the absence of local contamination can be guaranteed.

In the present study a special effort was made to reduce local influence on the aerosol sampling. A General Electric condensation nuclei counter was modified to decrease the time constant of the output signal for the measuring range to about 1 sec and to lower the detection limit to about 10/cm³. The signal from this counter controlled the pumps of the aerosol samplers. Sampling was turned on only when the total particle concentration at the entrance of the aerosol intake was 500/cm³ or below. A similar arrangement has been used by Maenhaut et al. (1977). Direct emissions from the diesel oil-fired power plant of the station and from local ground and air traffic caused concentration increases by two orders of magnitude or more above the average level of about 300/cm³. Therefore direct local influence on our samples can safely be excluded. During our experiment, between 50 and 98 % of each sampling period could be used for collecting locally uncontaminated particles.

Local contamination is not restricted to direct flow from the local sources to the measuring site. In extremely clean air masses without rapid elimination processes it is conceivable that local emissions are contaminating atmospheric measurement in aged form on indirect routes to the sampling site. Local or mesoscale circulation systems can bring aged emissions back to the source area within their residence time. We cannot prove the absence of indirect local contamination. However, during the course of the experiment a

number of observations were made which can be used as evidence:

1. The general level of the total particle concentration was in good agreement with results from other arctic measurements (Flyger et al. 1978) and with our understanding of the global background values
2. Even in periods of several days with strong winds from W-NW excluding any possibility of indirect local influence, the particle concentrations did not sink below the general level
3. While being on the background level ($300/\text{cm}^3$) the total particle counts usually exhibited extremely small (1–2 times the threshold value) temporal variations. During the few periods where indirect local contamination was suspected, rapid fluctuations (5–10 times the threshold value) appeared though the general concentration level remained low. Hence it was concluded that the stability of the total particle concentration could be used as an indicator for possible indirect (low level) contamination.

In Fig. 1 a section of the original Aitken nuclei recording is depicted showing both the stability of the low level particle concentrations and a period with direct local influence. The readings have to be multiplied by a factor of 2 to compensate for losses in the aerosol intake (Heintzenberg, 1980).

The combined results of particle concentration-controlled sampling and of the evaluation of the high-resolution Aitken nuclei recordings led us to the conclusion that our chemical results presented in the following sections are free from direct or indirect local contamination.

3. Experimental

3.1. Sampling and analysis

Sampling for chemical analysis was done by using 47 mm diameter membrane filter with $5\text{ }\mu\text{m}$ pore diameter for the total aerosol fraction and with 25 mm membrane filters for size-segregated sampling. The sequential filtration technique described by Cahill et al. (1977) employing two membrane filters in series was used. This sampler separates the aerosol particles into a coarse and a fine fraction. The flow rate used (5 l/min) yields a 50% aerodynamic cut-off radius $r_c \approx 0.5\text{ }\mu\text{m}$ according to Spurny and Lodge (1972) efficiency calculations, assuming a particle density of 2 g/cm^3 .

The filters for the total aerosol fraction were analyzed wet chemically for nine major constituents (Heintzenberg et al., 1979). However, results from Ca^{++} are not reported because of

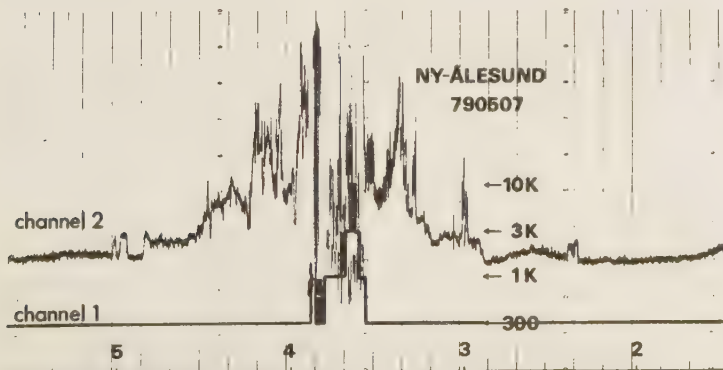


Fig. 1. Total particle concentrations at Ny-Ålesund, Svalbard, 1979-05-07. The numbers on the abscissa correspond to full hours. Channel 1 records the measuring range cm^{-3} . Channel 2 records relative particle counts in the actual range. Example: 0200 h the reading was 30% of range 300 = 90 cm^{-3} .

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excessive blank values. The analysis of the size-segregated filter for sulfur and trace metals was made using particle induced X-ray emission (PIXE) (Johansson et al., 1975). The consistency of the results obtained by the two analyzing methods was checked by comparing the sulfur concentrations for our experiment. These showed satisfactory agreement, having maximum deviations of about 20%. The accuracy and precision for most of the results obtained are well below 20%. However, results with uncertainties up to 30% have been accepted in the data evaluation.

Particle size distributions and optical properties were measured with a General Electric condensation nuclei counter, a 5-channel Royco-225 optical particle counter and a 6-channel integrating nephelometer. This part of the instrumentation is described in detail in Heintzenberg (1980).

3.2. Artifact formation in the filter sampling

During the collection of reactive aerosols and during aerosol sampling in the presence of reactive gases, chemical reactions on the filter surfaces can introduce serious errors in the measured concentrations (Klockow et al., 1979; Pierson et al., 1980). Especially the halogens can form volatile compounds which are lost during sampling. Eriksson (1960) proposed that chloride loss occurs as a consequence of pH-lowering reactions between seasalt particles and, e.g., H_2SO_4 which causes a supersaturation of aqueous HCl in the particles relative to the atmospheric pressure of HCl vapor,

resulting in volatilization of Cl as HCl. Klockow et al. (1979) have studied the loss of collected Cl and I when exposed to sulfuric acid. The relative amounts lost were influenced by filter type, relative humidity and the available amounts of hydrogen ions.

In Fig. 2 the concentrations of hydrogen ions are plotted versus chlorine for our Spitsbergen data. The chlorine concentrations appear to be inversely related to the hydrogen ion concentration. The size fractionated samples have lower losses especially in cases when the hydrogen ion concentration is low. Different artifact formation on the different filter materials used for wet chemical and PIXE analysis is one possible explanation. A second explanation is based upon the different formation mechanisms for chlorine-containing particles originating mainly from sea spray droplets and the hydrogen-containing particles of anthropogenic origin existing probably in the form of sulfuric acid or acidic sulfates. The sea spray generation mechanism will produce particles predominantly in the coarse fraction while the anthropogenic hydrogen will be found mainly in accumulation range particles (see Whitby, 1978, for definitions). Since the two ranges to a great extent will be sampled on different filters with the sequential technique, artifact formation with chlorine loss can be expected to be lower in this sampler than on the total filter sampler where all chemical species are accumulated on the same filter.

There are other possibilities of artifact formation, especially those involving SO_2 conversion. As data on gas phase components are lacking, we must assume that there was no artifact formation involving SO_2 or HNO_3 , etc.

4. Results

4.1. Chemical composition of arctic haze samples on Spitsbergen

Earlier measurements in the Arctic have shown very similar sulfate concentrations in northern Scandinavia, Spitsbergen and Alaska (Rahn et al., 1979c). Furthermore, these measurements show large seasonal variations, typically one order of magnitude for sulfate and vanadium (Rahn et al., 1979b). As reasons for the high winter values, they suggest the general winter circulation favoring south-north atmospheric transport to the Arctic

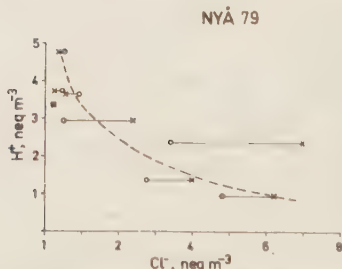


Fig. 2. Hydrogen equivalents plotted versus chlorine equivalents analyzed by wet chemically and PIXE (X), both filters added, in arctic haze samples at Ny-Ålesund, Svalbard, 1979-04-1979-05-08.

and the low arctic winter precipitation yielding long residence times for the arctic aerosol particles.

During our experiments at Ny-Ålesund 1979-04-19 to 1979-05-08 eight aerosol samples were collected covering time periods between 24 and 84 h. The results from the first sample were not included in the data evaluation because sampling was not yet controlled and contamination by heavy ground traffic nearby was suspected.

The results from the remaining seven samples showed a very stable absolute and relative aerosol composition. Most of the elemental concentrations varied less than 50% of their mean values, which is quite consistent with our results on the physical aerosol properties (see Table 2 in Heintzenberg, 1980). Especially the sulfate concentrations were very stable, varying less than 20% of the mean value. Chlorine concentrations exhibited the largest variability, up to one order of magnitude. However, the true variation cannot be separated from variations caused by the artifact discussed earlier. Vanadium is commonly used as a tracer for anthropogenic influence (combustion of heavy oil) in atmospheric aerosols. Unfortunately, we were not able to detect V in our own samples and refer to late winter measurements 1973-1974 at Ny-

Ålesund (NILU, 1977). Our grand average results are compared with averages from other locations in Table 1. The concentrations at the rural site are in general on the same level or slightly higher than those on Spitsbergen. Exceptions are iron, zinc and lead concentrations being 3-5 times higher at the rural site.

Concentration levels of urban aerosol in Copenhagen, Denmark (Flyger et al., 1976) are one to two orders of magnitude higher than on Spitsbergen, with the exception of sulfur being only 4-5 times higher in the urban aerosol. In the urban source area, a large fraction of the sulfur in the atmosphere is in the primary form of SO_2 , while in the arctic sink region a large part of the SO_2 can be expected to be transformed into particulate sulfate. Hence the relatively high particulate sulfur values on Spitsbergen do not necessarily reflect high pollution levels.

The South Pole is located near the center of the snow-covered Antarctic continent. Though it is much more isolated from tropospheric sources than any of the other remote locations considered, a comparison is somewhat complicated because of its height and the possibility of subsiding stratospheric air carrying sulfate particles to the surface.

Table 1. Average chemical composition of atmospheric aerosol samples at different locations. Concentrations are given in ng m^{-3}

Element	Urban Copenhagen*	Rural Velen†	Remote Summer South Pole‡	Remote Ny-Ålesund Late winter Spitsbergen§	Remote Summer N. Greenland
Na	—	—	3.3	130	—
Mg	—	—	0.72	51	—
Si	3700	—	—	110	43
S	3100	—	49	690	27
Cl	620	140	2.6	(96)	10
K	460	56	0.68	32	3.8
Ca	1600	58	0.49	73	9.1
Ti	70	4.1	0.10	<5.2	0.85
V	29	2.0	0.0013	0.29	0.12
Cr	7.5	3.0	<0.04	2.6	0.09
Mn	37	4.7	0.013	1.5	0.21
Fe	1200	61	0.62	64	6.4
Ni	11	1.3	—	0.7	0.08
Cu	25	2.0	0.029	<1.9	—
Zn	360	17	0.033	3.2	0.18
Pb	1700	16	0.076	<4.9	0.20

* Flyger et al. (1976). † Lannefors et al. (1979). ‡ Maenhaut et al. (1977). § Present work. || Flyger et al. (1978).
© NILU (1977).

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Hence, excluding S from the comparison yields values between 10 (Fe) and 150 (V) for the ratio north polar winter concentration/south polar austral summer concentrations and values between 2 (Cr) and 90 (V) for the ratio north polar summer concentrations/south polar summer concentrations. The extremely low vanadium concentrations in the south polar atmosphere indicate how effective the isolation of the location from anthropogenic sources is. Crustal weathering on the other hand seems to be a particle source common to both polar regions, which is somewhat surprising considering the extent of snow and ice coverage on the land masses. Fe comprises about 6% of the average crustal material and is found to be the dominating species of the metal components considered in the polar air samples. The lack of seasonal variation, which is confirmed by the agreement with mean annual concentrations found on Novaya Zemlya (Egorov et al., 1970), also indicates a local (crustal) source for Fe. Because of the lack of local crustal references, we refrain from a more detailed evaluation of the crustal component in our samples.

In earlier studies the seasonal variation of sulfur and vanadium in the arctic aerosol was reported. The summer results by Flyger et al. (1978) in northern Greenland (82.15°N, 29.88°W) can be used to give a rough idea about winter-summer variations for a large number of elements. The late winter Spitsbergen data are typically one order of magnitude higher than the summer Greenland data. Especially the known anthropogenically influenced elements such as sulfur, zinc and lead have 20–30 times lower concentrations in summer. These drastic seasonal variations are consistent with the

coupling-decoupling hypothesis proposed by Rahn et al. (1977) and with a first analysis of results from the Norwegian arctic measuring programme (Larsson et al., 1979). The central idea is that the Arctic is cut off or decoupled from the midlatitude source regions by the polar front in summer. In winter, on the other hand, the polar front lies just south of the midlatitude source areas.

This means that in winter transport to the Arctic is facilitated at the same time as atmospheric elimination processes along the pathways are less effective than in summer.

4.2. Ionic balance and molecular composition

As a means of checking the completeness of the chemical analysis, cation-anion balances were calculated for all samples. The results are listed on an equivalent basis in Table 2. Because of high blank values in the wet chemical analysis or because of the Cl-losses discussed in section 3, PIXE results have been used for the elements Cl, K and Ca. The sum of all analysed metals (M^+) also is taken from the PIXE analysis.

The fact that we always found an excess of cations might be attributed to phosphates and silicates missing in our analysis. As a relative measure of the completeness of the chemical analysis we calculated the parameter $\Delta = (\Sigma^+ + H^+ - \Sigma^-)/(\Sigma^+ + H^+ + \Sigma^-)$. The sum of all cations minus the anions yields the number of unbalanced charges which is compared to the total number of charges accounted for by our analysis. Δ is listed in the last column of Table 2. Our analysis yielded charge balance within about 10%.

The two charge-dominating ions are SO_4^{2-} and H^+ . If subtracting the sum of all cations from the

Table 2. Ionic balance on equivalent basis in aerosol samples taken at Ny-Ålesund, Svalbard, 1979-04-19–1979-05-08. M^+ stands for the sum of metal cations. $\Delta = (\Sigma^+ + H^+ - \Sigma^-)/(\Sigma^+ + H^+ + \Sigma^-)$. The values are given in neq/m³.

Sample	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Mg^{2+}	NH_4^+	M^+	Σ^-	Σ^+	H^+	Δ %
1	31.3	0.4	6.3	9.1	1.9	5.0	7.5	19.4	38.0	42.9	9.5	+16
2	43.1	2.0	0.6	1.8	0.2	1.6	16.2	2.1	45.7	21.9	36.9	+13
3	61.9	0.9	0.4	1.3	0.5	4.0	14.1	2.9	63.2	22.8	47.8	+6
4	41.9	0.3	0.2	1.9	0.7	2.1	9.2	3.9	42.4	17.8	33.5	+9
5	46.3	0.4	0.3	2.3	1.0	2.8	10.6	3.9	47.0	20.6	37.3	+10
6	33.1	0.3	4.0	9.1	1.0	5.4	6.4	5.4	37.4	27.3	13.8	+5
7	52.5	0.1	2.4	6.5	1.3	6.3	11.2	5.2	55.0	30.5	29.5	+4
8	45.6	0.6	7.1	11.7	0.9	6.7	8.6	4.0	53.3	31.9	23.5	+2

sulfate equivalents yields a residue of SO_4^{2-} , these ions must have protons as partners yielding sulfuric acid. Doing this in Table 2 indeed gives substantial amounts of sulfuric acid for all samples except number one which we classify as locally contaminated (mainly by metals).

The acidity of the arctic aerosol also can be discussed by just considering the measured pH-values. On the average, the H^+ concentrations were 32 ng/m^3 . In section 5.3 a total suspended dry mass of $4 \mu\text{g/m}^3$ is derived. There was no information on relative humidity available during the experiment. However, assuming the amount of water in the airborne aerosol particles to have the same magnitude as the dry particles, we derive a pH of about 2 for the airborne material. Hence our chemical analysis indicates that the arctic aerosol is very acidic, probably containing substantial amounts of sulfuric acid and acid sulfates.

5. Discussion

5.1. Air mass analysis

A trajectory analysis based upon isobaric 850 mbar 96 h back trajectories calculated by the Norwegian Institute of Meteorology did not yield conclusive results about the air mass origin. There are three reasons for this: (1) Ny-Ålesund lies in the N.W. corner of the trajectory grid system, (2) the meteorological information for the trajectory calculations is very limited in the arctic region, (3) Because of the small pressure differences in the Spitsbergen area only weak air movements occurred during the whole experiment. However, the finding that (as far as trajectories could be calculated) the air masses reaching the station had passed mainly over ice covered areas of the Arctic Ocean is noteworthy. Only during parts of samples 6 and 7 had the air passed over the Norwegian Sea and the northernmost parts of Scandinavia.

5.2. Chemical composition as a function of particle size

The average chemical composition of the haze particles is calculated in two size fractions divided at $r_c = 0.5 \mu\text{m}$ (see Table 3). The three major sources contributing to the arctic aerosol are the ocean, the earth's crust and anthropogenic sources. The first two produce mainly aerosols in the coarse particle range while the third is dominating the fine particle and accumulation modes. The marine source has a rather small influence because the air

Table 3. Average size segregated chemical composition of arctic haze samples at Ny-Ålesund, Svalbard, 1979-04-19–1979-05-08. Total suspended mass in accumulation range and coarse particle range are compared to results from inversion of optical data

Element or ion	Average concentrations, ng/m^3 Accumulation range	Coarse particle range
H	32*	—
NH_4	153*	—
NO_3	39*	—
Na	—	33 ¹⁾
Mg	—	49 ¹⁾
Si	41	68
SO_4	1850	220
Cl	(11)	(85)
K	15	17
Ca	21	52
Ti	<2.0	3.2
Cr	1.6	1.0
Mn	0.75	0.75
Fe	26	37
Cu	1.6	<0.32
Zn	2.6	0.58
Pb	3.0	<1.9
Chemical analysis (excl. sample 1)	$\Sigma 2200$	$\Sigma 650$
Inversion of optical data (grand average)	$\Sigma 3900$	$\Sigma 760$

* Results of total aerosol samples, assumed size segregation.

has passed mainly over ice-covered sea areas. Part of the SO_4^{2-} , Cl^- , Na^+ and to lesser extent Mg^{++} and Ca^{++} are probably of marine origin. According to the generation mechanism their major fraction lies in the coarse particle range. Typical soil derived elements are Si, Ca, Ti, Fe (and to some extent Mg, K, Cr and Mn). They also are found mainly in the coarse particle mode in accordance with their production process. SO_4 , NH_4 , NO_3 , Cu, Zn and Pb are associated predominantly with submicron aerosols in urban areas.

5.3. Comparison between chemical and optical analysis

The relationship between the light scattering coefficient σ_{sp} and submicron mass concentration m_{acc} or submicron sulfate concentration $(\text{SO}_4^{2-})_{\text{acc}}$

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has been used as an index of the role of submicron particles and especially sulfates in tropospheric optics. The ratios σ_{sp}/m_{acc} and $\sigma_{sp}/(SO_4^{2-})_{acc}$ have been determined for continental aerosols in many different locations (Waggoner et al., 1976; Waggoner et al., 1980). For the grand average results we find $\sigma_{sp}/m_{acc} = 3.9 \text{ m}^2 \text{ g}^{-1}$ which is in good agreement with previously reported data for industrial regions. The light scattering sulfate ratio at Ny-Ålesund is $8.3 \text{ m}^2 \text{ g}^{-1}$ which is near $10 \text{ m}^2 \text{ g}^{-1}$ reported by Waggoner et al. (1976) for St. Louis, Missouri.

The size distribution inverted from our optical measurements (Heintzenberg, 1980) can be written as mass size distribution assuming a density of 2 g cm^{-3} for the aerosol particles. This inverted mass distribution from the grand average of the optical data has been plotted in Fig. 3. In general inverted size distributions depend on the refractive index of the aerosol particles. The results of the chemical analysis can be explained assuming acid sulfate particles dominating arctic haze (see Tables 1–3). Therefore in the inversion we allowed the refractive index of the particles to vary between 1.36–0i (sulfuric acid) and 1.53–0i (ammonium sulfate). The corresponding variations in the inverted size distribution are marked as error bars in Fig. 3. Drawn as a histogram are the inversion results for the refractive index $1.5-0.005i$ which we consider to be a good approximation for background aerosol particles. The mass size distribution was integrated over the size ranges of our two-stage sampler. The results are compared with the mass results from chemical analysis in Table 3.

Both chemical and optical analyses yield 3–5 times more mass in the accumulation range than in the coarse particle range. The total suspended mass from chemical analysis is $3 \mu\text{g}/\text{m}^3$ compared to $5 \mu\text{g}/\text{m}^3$ from the inversion. The chemical status of the elements analysed by PIXE have not been taken into the calculations. Presumably many of the metals exist as oxides. A number of main components, i.e. C, Al, organics have not been determined. Adding those components to the mass chemically determinable would bring the optical and chemical total suspended mass concentrations into closer agreement. Furthermore, considering the fact that optical and chemical analyses are looking at completely different particle properties and both involve a number of assumptions, the agreement is quite satisfactory.

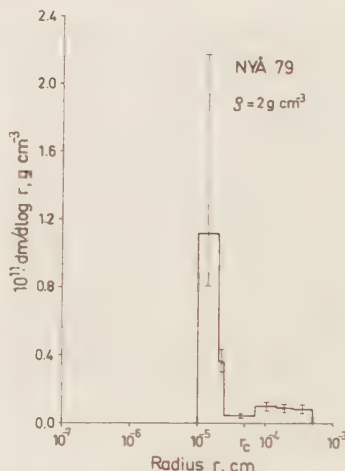


Fig. 3. Grand average mass size distribution inverted from optical measurements at Ny-Ålesund, Svalbard, 1979-04-19–1979-05-08. The density was assumed to be 2 g cm^{-3} . The results for $m = 1.5-0.05i$ are drawn as a histogram. The error bars show the variation of the results when allowing refractive index variations between $m = 1.36-0i$ (sulfuric acid) and $m = 1.53-0i$ (ammonium sulfate). r_c is the 50% cut off radius of the two-stage sampler for chemical analysis.

6. Conclusions

All evidence of previous studies of the composition and the origin of the arctic aerosol (see the review by Rahn, 1979c) suggests the anthropogenic pollution component dominating the winter aerosol in the Arctic. In this study, the combination of chemical composition, optical properties and size distribution data independently support this hypothesis. The mass size distribution determined by physical measurements has its sharp maximum in the accumulation range, indicating the presence of a well-aged aerosol. The results of the size fractionated chemical measurements show that S, Cu, Zn and Pb are found mainly in submicron particles. Long-range transport from anthropogenic, midlatitude source areas seems to be the only possible cause for these findings.

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ХИМИЧЕСКИЙ СОСТАВ АРКТИЧЕСКОЙ ДЫМКИ В НЮ-ЭЛЕЗУНД, ШПИТЦБЕРГЕН

В конце зимы 1979 г. в Нью-Элезунде на Шпитцбергене (12° в.д., 79° с.ш.) были собраны пробы частиц арктической дымки. Пробы с фильтров анализировались химически (в растворе) и ретигено-флюоресцентным методом. Были определены концентрации 17 основных ионов и атомов металлов, которые сравниваются с результатами предыдущих арктических и антарктических исследований. Одновременные измерения распре-

ления частиц аэрозоля по размерам использовались для проверки согласованности полученных результатов. Как химический состав, так и распределение по размерам поддерживают гипотезу, что зимний арктический аэрозоль испытывает большое влияние долгоживущего континентального аэрозоля, возникающего в областях антропогенных источников средних широт.

Paper VA COMPREHENSIVE STUDY OF PHYSICAL AND CHEMICAL PARAMETERS OF THE ARCTIC SUMMER AEROSOL;Results from the Swedish expedition Ymer-80

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A COMPREHENSIVE STUDY OF PHYSICAL AND CHEMICAL PARAMETERS OF THE ARCTIC SUMMER AEROSOL;

Results from the Swedish expedition Ymer-80

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Arrhenius laboratory, S-106 91 STOCKHOLM, SwedenABSTRACT

The Swedish icebreaker expedition Ymer-80 exploring the Norwegian part of the Arctic during the summer of 1980 offered unique opportunities for a coordinated atmospheric research program. Chemical and physical properties of the Arctic aerosol were studied using different kinds of samplers and continuous monitors connected to a common air inlet. Local contamination such as emissions from the ship and its helicopters were avoided using a condensation nucleus counter to control the sampling. Emissions from Arctic settlements were found to contribute only condensation nuclei and to have no significant influence on the aerosol mass and chemical composition. Arctic summer grand average levels, especially those of possible anthropogenic components i.e. soot, non-marine S, Ni, Cu, Zn and Pb, were lower by one order of magnitude or more than late winter levels as found on Spitsbergen, but on the same level as summer values on Northern Greenland. Most of the components varied over one to two orders of magnitude during the expedition. Sampling periods mainly influenced by sea spray were characterized by high TSP and chlorine levels. A few cases, possibly influenced by long range transport from the European continent, were characterized by high σ_{sp} , soot, sulphur and heavy metal concentrations. The Arctic background aerosol composition was found to be determined by the relative strength of active source and sink mechanisms in combination with the sampling time resolution.

INTRODUCTION

The influence of midlatitudinal anthropogenic sources on the Arctic aerosol have been found to be strong during the winter period (Rahn and Shaw 1978 and

Rahn and McCaffrey 1980). According to Rahn's coupling-decoupling hypothesis, the Arctic region is coupled to the Eurasian continent during the winter (i.e. the meteorological conditions are more favourable for air mass transport from midlatitudinal large source regions into the Arctic). A low winter precipitation increases the atmospheric residence times. This enables air pollutants transported to the Arctic region to accumulate there. According to Rahn's hypothesis the Arctic is decoupled during the summer when the precipitation is also somewhat higher which implies lower air pollution concentrations. In fact winter values of a number of air pollution indicators (e.g. turbidity, non-marine boron, manganese and vanadium etc.) as measured in Northern Alaska are an order of magnitude or more above summer values. Measurements of physical and chemical properties of airborne particulate matter during the summer on Northern Greenland (Flyger and Heidam 1978) also indicate very low concentrations compared with those measured in late winter on Spitsbergen (Heintzenberg 1980 and Heintzenberg et al 1981).

The Arctic summer air has the lowest air pollution levels. Because of the potential influence on the energy balance it is interesting to study the chemical composition of this atmosphere. It is also of great importance to obtain reliable measurements of as many components as possible, especially those linked to human activity, before oil drilling activities start in these areas. Such activities could drastically increase the emissions in the Arctic shelf regions. An example of the rapid change in the Arctic during recent decades is that the population north of the Arctic circle tripled between 1940 and 1975 (CIA 1978).

To the memory of A.E. Nordenskiöld's discovery of the north east passage in 1878-79 a scientific expedition, using the Swedish icebreaker Ymer as research vessel, was undertaken in the summer of 1980. One of the larger efforts was the atmospheric (chemistry and physics) program which included several research groups from Sweden, Western Germany and the U.S. Through extensive measurements the chemical and physical properties of the Arctic summer aerosol (and trace gases) were to be determined, leading to information about possible sources and sink mechanisms.

EXPERIMENTAL

The first leg of the expedition operated from July 5 to August 4 in the area between Spitsbergen and Franz Joseph land as shown in Fig 1. The second leg

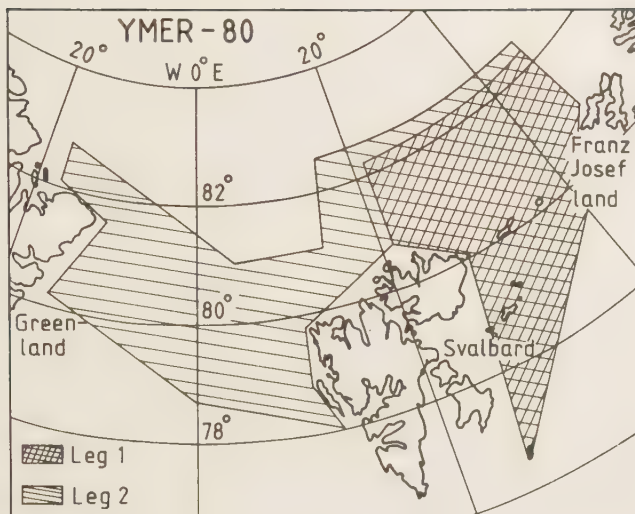


Fig 1. Working areas during the two legs of the expedition.

covered the area between Northern Greenland and Franz Joseph land from August 10 to September 22, 1980 (see Fig 1). The atmospheric program was placed on the third deck 16 meters above sea level in two containers, one for pumps and the other for the sampling equipment (see Fig 2). The air intake consisted of a 5 meter long vertical 15 cm diameter polythene pipe with a hood on top to prevent droplets and snow flakes from entering. The pipe was bent 90 degrees in order that it should enter the sampling container horizontally from the front. The design and positioning of the pipe was based on smoke-generation studies of the turbulence on the forward side of the bridge. The risk of contamination from resuspended material deposited on the fore deck was thus minimized and the influence from sea spray created at the bow reduced.



Fig 2. Photograph of Ymer in the Arctic ice. Close-up of pump container (first from right) and sampling container (second from right) with the black inlet pipe.

The samplers were mounted along the pipe inside the container as shown in Fig 3. Isokinetic sampling using specially designed plexiglass inlets was employed for those samplers where the coarse fraction (particles $>2\ \mu\text{m}$) was of interest. Table 1 contains a list of the aerosol samplers connected to the pipe.

Emissions from the icebreaker's diesel electric engine and activities related to the other scientific programs such as helicopter search for polar bears and leads in the packice, represented strong sources of contamination. In order to avoid contamination the sampling was controlled by a TSI 3020 condensation nuclei counter (CNC) which turned off all samplers when a preset concentration level was exceeded. A fast response control signal was taken directly from the photodiode to detect stack emissions while a slow response signal from the sampling output was used to indicate changes in the general level of condensation nuclei (CN) concentration. After each switch-off a 5 minute delay was added to clean the whole sampling system. The CN-concentration is a very sensitive indicator of recent emissions of combustion aerosol where the particles have not yet coagulated into the accumulation mode (particles in the $0.05 - 2\ \mu\text{m}$ diameter range). The composition of the smoke emitted from the diesel engines was measured at the top of the stack using total filters. The problem of possible local indirect contamination is discussed later.

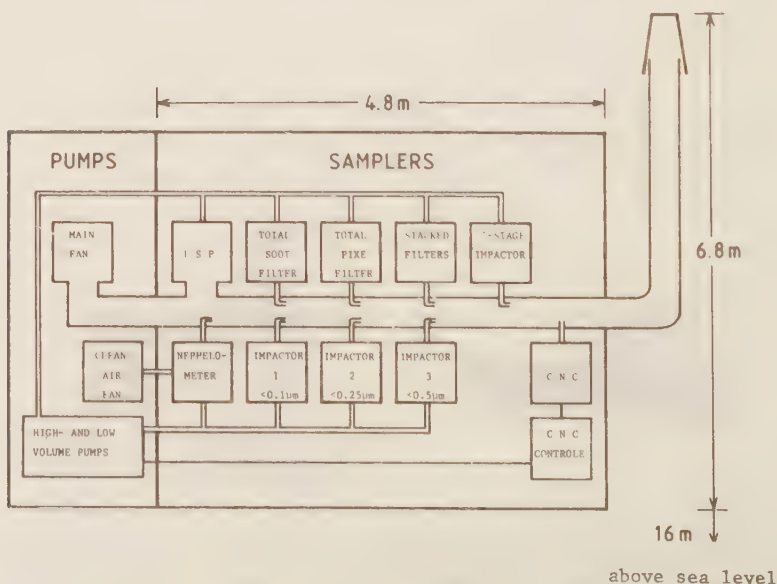


Fig 3. Schematic figure of the air intake and samplers.

Table 1. Characteristics of samplers.

Instrument	Sampling media	Measured aerosol parameter	Diameter range	Analytical technique	Reference
High volume sampler	142 mm Ø ZEFLUOR 2 µm pore size	Total suspended particulate mass	< ~ 20 µm	Gravimetric	
Total soot sampler	47 mm Ø MICROSORBAN filter	Total mass of soot, light absorption coefficient	< ~ 20 µm	ISP (Integrating sphere photometer)	Heintzenberg (1982)
Total PIXE sampler	25 mm Ø ZEFLUOR 2 µm pore size	S, Cl, Metals	< ~ 20 µm	PIXE (Particle Induced X-ray Emission)	Johansson et al (1975)
Stacked filters	25 mm Ø NUCLEPORE 8 µm pore size	S, Cl, Metals	> 2 - 3 µm	PIXE	
	25 mm Ø NUCLEPORE 0.4 µm pore size	S, Cl, Metals	< 2 - 3 µm	PIXE	
7-stage Battelle cascade impactor	Polystyrene with evaporated paraffin	S, Cl, Metals	> 8 µm, 4 - 8 µm	PIXE	
	25 mm Ø NUCLEPORE 0.4 µm pore size		2 - 4 µm, 1 - 2 µm 0.5-1 µm, 0.25-0.5 µm		
Integrating nephelometer	---	Light scattering coefficient at 0.55 µm wavelength	< 0.25 µm		
			mainly 0.2 - 1 µm	Photon counting	Charlson et al (1974)
Winkler impactors	47 mm Ø MICROSORBAN 15 mm Ø ZEFLUOR 2 µm pore size	Mass of soot, S	< 0.2 µm < 0.5 µm < 1 µm	ISP and PIXE	
Condensation nuclei counter, TSI 3020	---	Particle concentration per cm ³	0.004 - 0.2 µm	Optical counting of single droplets	Bricard et al (1976)

RESULTS

The time series of a number of aerosol parameters measured during the Ymer-80 expedition are shown in Fig 4. The length of the measurement periods depends on both the prevailing aerosol concentrations and the sampling efficiency i.e. the ratio of actual sampling time to total length of the measurement period. The duration of the measurement periods ranged from 8 hours to a week and the sampling efficiency from 30 to almost 100%. The time constant of the variations appear to be of shorter duration than the measurement periods since often no trends can be resolved in the time series. Therefore it is probable that larger variations should be exhibited if the time resolution of the measurements were increased. In the present results variations of up to two orders of magnitude were found for many of the parameters, which is far larger than the errors in sampling and analysis, being typically of the order of 20% or less.

Time weighted averages have been calculated and are shown in Table 2. Samples 3, 4, 14, 20, 21 and 23 were excluded from the grand average and the monthly averages since they were either taken outside the working area shown in Fig 1 or were contaminated (no 4 and 23). Samples representative of seaspray, long range transport and background aerosol have been averaged and are shown in separate columns.

Comparisons in Table 2 indicate that the Ymer grand average concentrations are about the same as summer Northern Greenland values except for chlorine which is much higher, due to the influence of the ocean. Arctic winter levels measured on Spitsbergen are one order of magnitude higher for parameters which are possible pollution indicators i.e. σ_{sp} , soot, non-marine S, Ni, Cu, Zn and Pb. Non-marine concentrations are obtained by subtracting the marine component calculated from bulk sea composition using Cl as tracer. It is interesting to note that the primary aerosol constituents soot, Fe, Ni, Cu, Zn and Pb have a larger winter to summer ratio than the secondary constituent S. Eastern United States rural summer concentration levels are one to two orders of magnitude higher than the Ymer levels. The largest differences are found for soot and lead while the lowest differences are found for components such as K, Ca, Ti and Fe which are often associated with soil erosion.

Size distributions of sulphur representing local contamination, Arctic summer background, long range transport and long range transport as measured in southern Sweden are plotted in Fig 5. In some of the graphs the soot size distribution is also plotted.

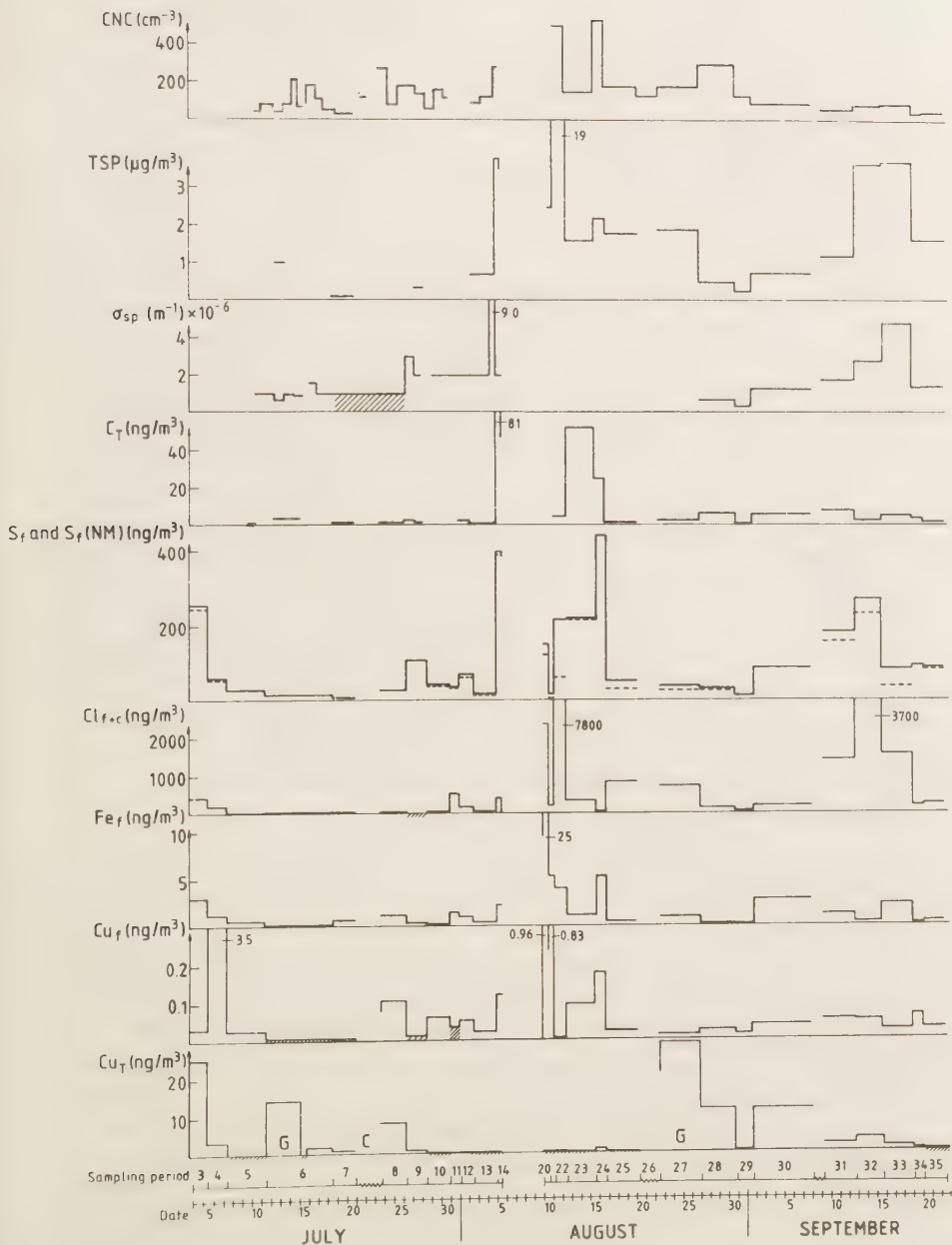


Fig 4. Concentration versus time for nine of the measured aerosol parameters. TSP denotes total suspended matter, σ_{sp} the scattering coefficient and C total elemental (graphitic) carbon. Index T^{sp} indicates total fraction, f indicates accumulation mode, c indicates coarse mode and NM means non-marine component (marked with broken lines - - - in case of S). ///// indicates detection limit. In the Cu_T time series G shows incidents of garbage burning and C

Table 2.

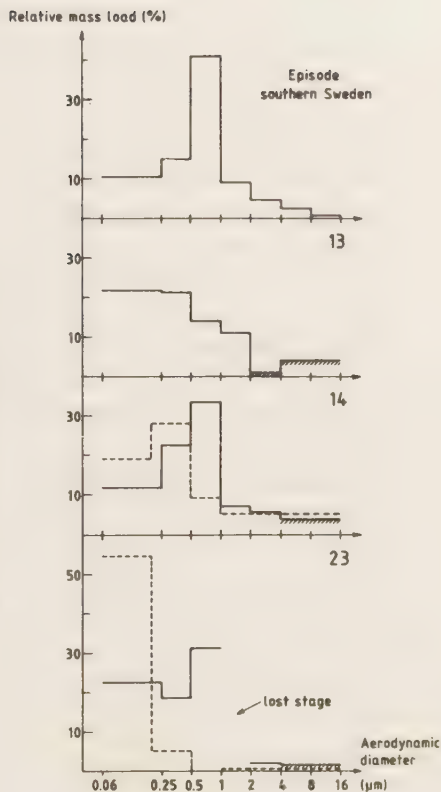
Time weighed monthly and grand averages compared to measurements at other remote locations. Concentration averages of samples representing seaspray, long range transport and background are also listed.

Parameter	Unit	1)			2)			3)			Ymer-80				Sample numbers		
		Great Smokey Mts	Ny-Ålesund	Northeast Greenland	Grand average	July	August	September	22+33 Seaspray	14+24 Long range transport	7+29 Arctic background						
CN	cm ⁻³	--	380	200'	130	100	240	76	270	390	80						
TSP	µg/m ³	30	4.7	--	1.9	0.39*	3.1	1.8	11	3.0	0.17						
σ _{sp}	x10 ⁻⁶ m ⁻¹	--	15	--	1.5	1.1	1.6*	1.9	4.8 ^{\$}	9.0 ^{\$}	0.68						
C _T	ng/m ³	1100	70	--	4.5	1.9	5.7	4.5	5.5	53	1.3						
S _f	"	3700	620	27	99	42	100	130	150	300	13						
S _{fNM}	"	3700	620	26	82	41	76	110	53	300	13						
Cl _{f+c}	"	< 17	96	10	910	45	1200	1200	4700	240	53						
K _{fNM}	"	40	15	3.8	2.6	1.2	1.7	4.0	45 [£]	4.4	0.59						
K _{afNM}	"	16	21	9.1	2.7	3.4	2.1	2.8	42 [£]	7.3	2.2						
K _{if}	"	< 2	< 2.0	0.85	0.16	<0.063	0.22	0.17	0.37	<0.26	0.045						
K _{ef}	"	28	26	6.4	1.1	0.54	1.4	1.3	3.3	4.0	0.41						
K _{if}	"	1	< 0.36	0.08	<0.058	<0.027	<0.025	0.10	0.058	0.56	<0.032						
K _{uf}	"	3	1.6	--	0.041	0.033	0.054	0.036	0.015	0.34	0.007						
K _{nf}	"	9	2.6	0.18	0.14	0.11	0.23	0.084	0.071	0.93	0.036						
K _{bf}	"	97	3.0	0.20	0.14	<0.097	0.30	0.056	0.14	1.56	<0.031						

Geometric mean of Aitken nuclei, * based only on 3 samples, \$ only sample 14, £ only sample 33, including marine component

) Stevens et al 1980, 2) Heintzenberg et al 1981, 3) Flyger and Heidam 1978

Fig 5. Sulphur (—) and soot (---) size distributions taken during the Ymer expedition, compared with an average size distribution obtained from measurements in southern Sweden during episodic conditions, i.e. long range transport from Western Europe. The size fractions of the cascade impactors include two open intervals: $>8\text{ }\mu\text{m}$ and $<0.25\text{ }\mu\text{m}$. In order to present these intervals graphically an upper size limit of $16\text{ }\mu\text{m}$ and a lower size limit of $0.06\text{ }\mu\text{m}$ were chosen. In the same way 2 and $0.06\text{ }\mu\text{m}$ have been chosen as upper and lower size limits in the case of the soot distributions. ///// indicates detection limit. It should be pointed out that the column area reflects the relative mass load on each stage.



DISCUSSION

The Arctic summer aerosol exhibited an unexpectedly large variability in size distribution and chemical composition. In order to better understand the cause of the variations several sampling periods were selected for further evaluation. Thus we will discuss separately the characteristics of emissions from different sources, how they can be distinguished and how local contamination can be identified and accounted for.

Indications of direct and indirect local contamination

Atmospheric studies in the Arctic generally pose great demands on the sampling routines to ensure uncontaminated samples. When using a 22 000 horsepower

icebreaker as a research platform those demands must be set even higher. In order to be able to identify contributions from the icebreaker's diesel engines, total filter samples were taken from one of the five exhaust pipes. The composition is given in Table 3. The ratios between smoke and Arctic summer accumulation mode concentrations (see Table 3) are indicators of the dilution that has to take place to reduce each m^3 (of about 500 m^3 flue gases emitted per minute) of the ships emissions to Arctic summer concentrations. Since the exhaust concentrations also include coarse mode particles the ratios should be regarded as upper limits as if the smoke was only confined to accumulation mode particles.

Table 3. Measured total elemental and soot concentrations in emissions from one of the ship's five diesel engines. Ratios to Arctic summer accumulation mode concentrations are also included.

Parameter	Diesel smoke concentration§	Diesel smoke Arctic summer(1)	Diesel smoke Arctic summer(2)
CN(cm^{-3})	$1 \cdot 10^9$ §	$5 \cdot 10^6$	$8 \cdot 10^6$
C _T	13 000	—	$3 \cdot 10^6$
S	400	15 000	4 000
Cl	<40	<4 000	<44
K	<30	<8 000	<12 000
Ca	<40	<4 500	<15 000
Ti	<10	<12 000	<65 000
Fe	<10	<1 500	<9 000
Ni	<0.5	<6 000	—
Cu	0.5	—	13 000
Zn	1.0	5 500	7 000
Pb	<0.6	<3 000	<4 500

§ in $\mu\text{g}/\text{m}^3$, § estimated

1) Flyger and Heidam 1978

2) this work

The most sensitive indicators of the ship's emissions are those components having the highest ratios i.e. soot and CN while the metals are two orders of magnitude less sensitive to smoke contamination. The sulphate (as sulphur) ratio is of the same magnitude as those of the metals. Since sulphate is gradually produced from its gaseous precursor, sulphur dioxide, the relative and absolute sulphate contribution in the smoke plume will change with the age

of the plume. Therefore it is difficult to estimate the sensitivity of sulphate as a plume indicator. An instrument continuously measuring either CN or soot and operating with a short time constant would therefore be ideal to protect the air sampling on board. A recently developed CNC (see Table 1) fulfilled these criteria and was used to control the sampling system as described earlier.

Aerosol formation in emissions from high temperature sources e.g. diesel combustion, results in very fine particles in the nucleation mode (particles with a diameter $< 0.05 \mu\text{m}$) growing through coagulation (Whitby 1978) into the accumulation mode. High concentrations (measured by a CNC) of very fine particles resulting in a very small mass median diameter can therefore be used to identify freshly formed aerosols. The size distribution of soot (graphitic carbon) was measured in four stages (see Table 1) and can thus be used to identify sampling periods with possible contamination from the ships emissions. Very high soot concentration, of which 90% was found in particles with a diameter less than $0.2 \mu\text{m}$, was experienced in sample 23. The typical relative soot fraction in the size range below $0.2 \mu\text{m}$ particle diameter is 30% which is also the late winter average as measured at Spitsbergen (Heintzenberg in press). On this basis sample 23 was excluded as being contaminated. Of course this reasoning concerning soot (very-fine-particle concentration as fresh aerosol indicator) also applies to other primary aerosol constituents e.g. Ni, Cu and Zn.

Indirect contamination i.e. aerosols emitted by the ship or the helicopters not directly entering the sampling system but allowed to age (thus transforming the particle size distribution towards larger particles) can probably not be identified using the above mentioned criterium. However, using the ratios of metals to soot one can infer that, if the soot values are reasonably low and therefore probably not contaminated, the metals are with an even higher probability uncontaminated. As mentioned earlier this reasoning may not be applicable to sulphate.

Garbage, mostly packaging materials, was burned on two occasions. Although placed on the leeward side turbulence from the ship's body caused particulate emissions to contaminate the ship and the upper parts of the sampling line. When restarting sampling some of this material became resuspended and contaminated especially the large particle collectors of the isokinetic samplers. As an indicator of such contamination the copper concentrations as measured by a total filter sampler are shown in Fig 4, where the garbage fires

are marked with G. In order to avoid further resuspension the sampling pipe was taken apart and cleaned (C in Fig 4). Unfortunately not all material was removed but rather loosened and resuspended during the subsequent sampling interval.

Aerosol blank samples i.e. air going through the main line but all sampling pumps switched off, were taken during two periods. Samples "exposed" this way are compared with non-exposed blanks in Table 4 to reveal whether aerosol particles enter the samplers during periods when the CN-level is exceeded and the sampling pumps are shut off. The results show additional material or blank content variation of the exposed blanks exceeding one standard deviation of the non-exposed blanks only for the elements S and Zn.

Table 4. Comparison of "exposed" (fan sucking air through main line, samples in position but sampler pumps switched off) and non-exposed blanks for elements detected.

Parameter	"Exposed" samples		Non-exposed blank	(ng)
	26	36	Average $\pm$ one sigma	
TSP	1.70095§	1.68031§	1.7011§(26) 1.67942§(36)	
C _T	0.036*	0.037*	0.038*	
S	45	52	44 $\pm$ 4.8	
Cl	29	12	25 $\pm$ 5.8	
Ca	7.4	11	10 $\pm$ 2.1	
Fe	9.9	8.7	9.4 $\pm$ 1.0	
Ni	<0.42	0.54	0.47 $\pm$ 0.080	
Cu	<0.42	0.55	0.56 $\pm$ 0.11	
Zn	0.36	0.43	0.37 $\pm$ 0.023	

§ filter weight in g, * optical density measured in the soot photometer

Emissions from Arctic settlements

Arctic settlements and human activities producing air pollution are insignificant compared with midlatitudinal sources. However, the remoteness of the Arctic in combination with the summer decoupling can make the anthropogenic emissions within the Arctic region important for the summer concentration levels found. Jeanicke and Schütz (in press) propose the settlements and related activities to be the main source of condensation nuclei (CN) during the Arctic summer.

A close study of those sampling periods having comparably high and relatively invariable CN-concentrations reveals that they are taken mostly during periods when ground level trajectories (Jaenicke and Schütz in press) indicate that Arctic settlements can have contributed to the aerosol concentration. Examples of such samples are 6, 8, 24, 25, 27 and 28 while samples 14 and 22, although having relatively high CN-concentration, can be related to long range transport and seaspray respectively as will be discussed later. A comparison with the other parameters in Fig 4 shows that high CN values do not in general correspond to high values of light scattering, soot or fine particle elemental concentrations. This implies that Arctic sources do not contribute a large amount to the light scattering, soot or elemental concentrations i.e. these emissions do not drastically alter the accumulation mode aerosol composition.

Seaspray

Seaspray is generated when air bubbles mixed in the water ascend and traverse the surface, thus producing droplets of different sizes (see e.g. Blanchard and Woodcock 1980). Using a ship as a sampling platform will add sea spray droplets produced from splashing at the bow, even when breaking ice. Two sampling periods were found to be mainly influenced by sea spray, one representing mainly the first production mechanism while the second is a mixture of both mechanisms. Sample 22 was taken just north of Kong Karls land in open water at one position and with an average wind speed of 12 m/s. Sample 33 was taken mainly in heavy pack ice while the ship was moving north west of Franz Josef land. The average wind speed was 6 m/s.

Characteristics of sea spray as found in those two samples (see Table 2) are: high TSP, σ_{sp} , Cl, K and Ca and normal CN, C_T and most of the metal concentrations. As shown both by σ_{sp} and the accumulation mode elemental concentrations, sea salt contributes considerably to the accumulation mode aerosol mass. The TSP concentrations are lower than predicted by Lovett (1978) for 15 m above the sea surface, but can mostly be explained by sea salt using Cl as a tracer and adding proportionally Na, Mg, S, K and Ca. In Table 5 ratios to the sea salt indicator chlorine are calculated for samples 22 and 33. S, K, Ca and Br to Cl ratios are on the same level as for bulk sea water composition. However, in sample 33 Br show some deficit while there is some evidence for an additional contribution of sulphur in both samples. The heavy metals all have ratios several orders of magnitude too high and therefore must have their main contributions from other sources.

Table 5. Sea salt characteristics and composition relative to chlorine compared with bulk sea water composition for the accumulation + coarse fractions of the two stage filter sampler.

Parameter	Sample 22	Sample 33	Bulk sea
Sea salt§ ($\mu\text{g}/\text{m}^3$)	30	10	-
TSP ($\mu\text{g}/\text{m}^3$)	19	3.9	-
CN (cm^{-3})	460	89	-
σ_{sp} (10^{-6} m^{-1})	&	4.8	-
C_{T} (ng/m^3)	5.3	5.6	-
Cl (ng/m^3)	7 800	1 600	-
Cl/TSP	0.41	0.41	0.55
S/Cl	0.075	0.063	0.047
K/Cl	0.028	0.017	0.021
Ca/Cl	0.027	0.021	0.021
Fe/Cl	0.0021	0.0030	$7 \cdot 10^{-7}$
Zn/Cl	0.00042	0.00023	$7 \cdot 10^{-7}$
Br/Cl	0.0028	0.0015	0.0035
Pb/Cl§	$8 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-9}$

§ Lovett (1978), & nephelometer not working, § accumulation mode.

Possible influence of long range transport

According to earlier discussions the Arctic region is more or less decoupled and should therefore experience few occurrences of long range transport from midlatitudinal source areas during the summer. Trajectories calculated by the Norwegian Meteorological Institute to Northern Norway, Bear Island and Spitsbergen show that these areas are only exposed to air parcels originating in central Europe during a minor part of the time in the summer (see Table 6). Average concentrations (see Table 2) of soot and the heavy metals (except Ni) were highest in August. This might be related to the higher frequency of central European origin trajectories experienced in August at both Spitsbergen and Bear Island (Table 6). During the Ymer-80 expedition only 2 or possibly 3 occurrences of long range transport were observed. It was not possible to clearly identify these events during the expedition. The first event took place at the very end of the expedition's first leg just after having left the working area as shown in Fig 1. The duration of this episode was only a few hours during the night of the fourth and the fifth of August. Corresponding surface and 850 mbar back trajectories calculated by Schütz (Jaenicke and Schütz in press) are shown in Fig 6. Sample 14 surface trajectories indicate

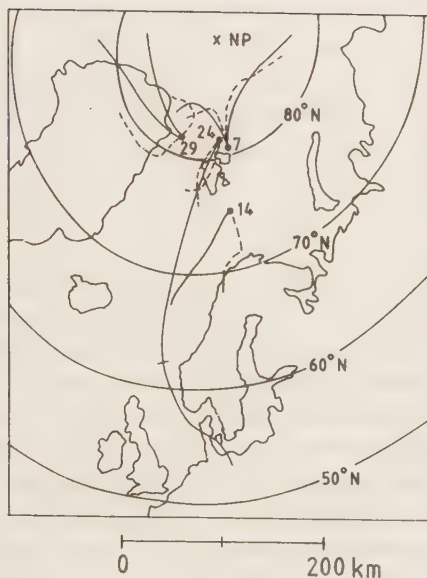


Fig 6. Isobaric 48 hour trajectories calculated at the surface (---) and at the 850 mbar level (—) by Schütz for samples 7, 14, 24 and 29. In cases where a significant change in the trajectory direction was observed, trajectories representing the start and end of the sampling period have been plotted. The sample 24 850 mbar trajectory (72 hours) was calculated by the Norwegian Meteorological Institute and closely resembles that calculated by Schütz (for the first 48 hours).

possible contributions from Northern Norway while the 850 mbar trajectory indicate possible contributions from further south. The second episode was experienced north east and north of Spitsbergen during sampling periods 23 and 24 on the second leg. As mentioned earlier 23 is probably contaminated by emissions from the ship while 24 shows no indications of such contamination. However, as seen in Fig 6 the air masses reaching Ymer during sample period 24 have passed over Spitsbergen. According to earlier discussions Arctic sources cannot be responsible for the comparably high levels of C_T , non-marine S, Ni, Cu, Zn and Pb measured during this period. Indications of long range transport from air mass history, with a possible origin in European Russia were found for samples 31 and 32. High levels of σ_{sp} , C_T and non-marine S supported this hypothesis. However the sea spray concentration was also very high, complicating the identification of an aerosol long range transport component.

Table 6. Average (October 1978 - September 1981) relative part of the time when trajectories on the 850 mbar level originating in central Europe reached the receptor-stations.

Location	July	August	September	(%)
Jergul, Northern Norway	14	9	8	
Bear Island	4	9	4	
Ny-Ålesund, Spitsbergen	1	4	2	

Characteristics of "long range transport" as measured in samples 14 and 24 (see Table 2) are: high levels of C_T , non-marine S and metal concentrations with elevated levels of CN, TSP and σ_{sp} . In addition increased levels of radon and radon-daughters reported by C. Samuelsson, Department of Radiophysics, University of Lund (unpublished data), indicate a continental non permafrost origin of the air masses. The relative increase in concentration levels during a long range transport episode compared with the Arctic "background levels" (discussed below) and the grand average are listed in Table 7. TSP, σ_{sp} , C_T , non-marine S, Ni, Cu, Zn and Pb have the highest ratios and are thus the most sensitive pollution indicators of long range transport influence. Sea spray can contribute considerably to TSP and σ_{sp} as seen previously. Therefore they are not useful as such indicators.

Table 7. Relative increase in long range transport (LRT) concentrations compared with Arctic "background levels" (ABL) and the grand average (GA), respectively. Accumulation mode concentrations are indexed with f, coarse mode with c and the non-marine component with NM.

Ratio	CN	TSP	σ_{sp}	C_T	S_{fNM}	CL_{f+c}	K_{NM}	Ca_{NM}	Ti	Fe	Ni	Cu	Zn	Pb
<u>LRT</u>	4.9	18	13	41	23	4.5	7.5	3.3	<5.8	9.8	>18	49	26	>50
<u>ABL</u>														
<u>LRT</u>	3.0	1.6	6.0	12	3.7	0.26	1.7	2.7	<1.6	3.6	>9.7	8.3	6.6	11
<u>GA</u>														

A comparison of four sulphur and two soot size distributions is presented in Fig 5. Sample 14 representing long range transport has a definite peak in the 0.25 - 1 μm particle diameter range for both sulphur and soot. A sulphur peak in the same interval can also be discerned in sample 23 which in addition also has finer sulphur containing particles, probably originating from the ship's emissions, as proposed earlier. This is supported by the soot size

distribution having 90% of the concentration on particles finer than $0.2 \mu\text{m}$ diameter. In fact the sulphur size distribution can be interpreted as a combination of two size distributions with mass median diameters in the intervals $<0.25 \mu\text{m}$ and $0.5 - 2 \mu\text{m}$, respectively. Sample 13 taken immediately before 14 has a quite different, flatter size distribution. It is also interesting to note the resemblance of the long range transport sulphur size distribution obtained in southern Sweden to that obtained in the Arctic (no. 14).

Arctic background levels

Background levels are often referred to as baseline concentrations when discussing the degree of pollution at a particular measuring site. Here we propose an operational definition that the samples having the lowest concentration levels and least risk of contamination represent the Arctic "background levels". Samples 7 and 29 fulfil these requirements. The main part of sample 7 was taken in air masses circulating around a weak high pressure center over the North Pole and represents an extremely aged air mass. In Fig 6 trajectories representing the onset and end of the sampling period show that the trajectories gradually turned from north east to north west. The ship was situated north east of Spitsbergen. The second "background" sample (no 29) was taken in air masses traversing North Eastern Greenland (see Fig 6) during sampling off the North Eastern Greenland coast. The average background levels taken as the mean of sample 7 and 29 are compared with levels experienced during long range transport and the grand average in Table 7. The background levels of potential air pollutants such as C_T , S, Ni, Cu, Zn and Pb are between one and two orders of magnitude lower than during episodic conditions. The difference compared with the grand average is generally one order of magnitude.

The variations of CN-concentration and σ_{sp} during sampling period 29 can be studied in detail in Fig 7. Rather high CN-values were experienced at the onset of sampling when some influence from Station Nord (a Danish military base situated in North Eastern Greenland) caused the sampling to be shut off for a few hours on the morning of August 31. As pointed out in the diagram passing banks of fog (C in Fig 7) causes the CN-concentration to drop one order of magnitude or more, reaching extremely low values of only a few particles per cm^3 . The variations of σ_{sp} are within one order of magnitude, roughly between 10^{-7} and 10^{-6} m^{-1} , which is much less than the

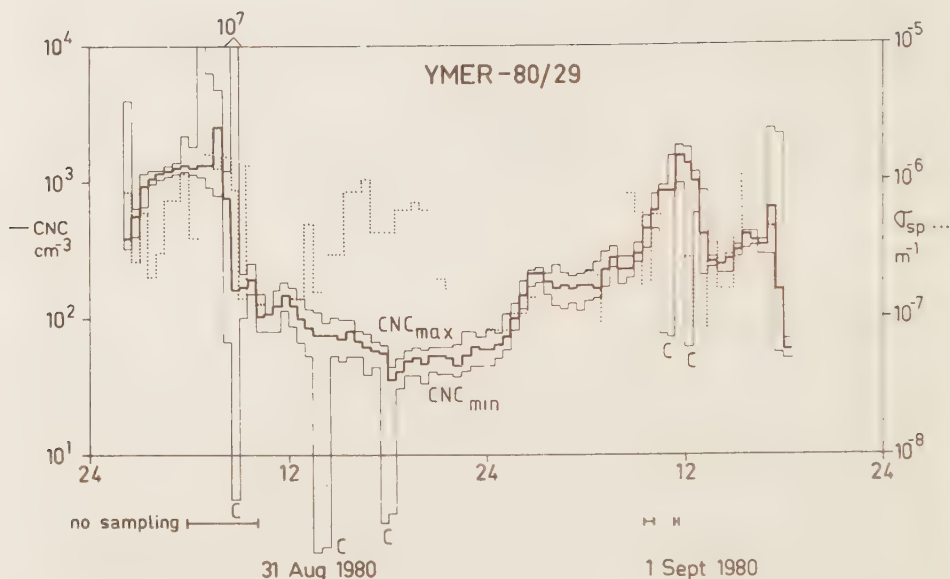


Fig 7. Variation of CN-concentration and σ_{sp} of sample 29. The area between maximum and minimum CN-values for each 30 minute sampling period is marked as a shaded area about the median (strong line). The time resolution of the nephelometer is ca. 30 minutes. The occurrence of fog banks or precipitation is marked with a C.

CN-concentration variations. The correlation between CN and σ_{sp} is not very high as can be seen in Fig 7. It should also be noted that the influence from Station Nord cannot be traced in σ_{sp} , which confirms the previous reasoning and anticipations of the minor risk of accumulation mode contamination from Arctic settlements.

SUMMARY AND CONCLUSIONS

As a consequence of a strict adoption of Rahn's coupling - decoupling hypothesis, low and constant levels of especially the anthropogenic aerosol components should be expected in the Arctic during the summer season. The Arctic summer ground level aerosol composition exhibited variations for most of the measured physical and chemical parameters of one to two orders of magnitude. The variation time constant appeared to be of shorter duration than

the measurement periods which were typically one to two days. Much of the variations can be explained by influence from aerosol long range transport, seaspray and settlement emissions in combination with the varying strength of scavenging mechanisms. The characteristics of different source types are summarized in Table 8.

Table 8. Rough characteristics of different source types influencing the Arctic aerosol composition.

Parameter	Ship's emissions	Settlement emissions	Long range transport	Sea spray
CN	H	H	I	I
TSP	-	L	I	H
σ_{sp}	-	L	H	H
C_T	H	L	H	I
S_{NM}	H	L	H	H*
Cl	L	L	L	H
Heavy metals	H§	L	H	I or L

* including marine component, § Cu and Zn

H = high, I = intermediate and L = low level

From the experience gained in this study we conclude that the mysterious background aerosol often referenced as a hypothetical lower limit content aerosol, does not exist. The lowest levels measurable i.e. the "background aerosol" are just a function of source and sink mechanisms in combination with obtainable measurement time resolution.

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